



Heriot-Watt University  
Research Gateway

## Rheology of lime pastes with biopolymer-based additives

### Citation for published version:

Arizzi, A & Banfill, PFG 2019, 'Rheology of lime pastes with biopolymer-based additives', *Materials and Structures*, vol. 52, no. 1, 8. <https://doi.org/10.1617/s11527-019-1310-8>

### Digital Object Identifier (DOI):

[10.1617/s11527-019-1310-8](https://doi.org/10.1617/s11527-019-1310-8)

### Link:

[Link to publication record in Heriot-Watt Research Portal](#)

### Document Version:

Peer reviewed version

### Published In:

Materials and Structures

### Publisher Rights Statement:

This is a post-peer-review, pre-copyedit version of an article published in Materials and Structures. The final authenticated version is available online at: <http://dx.doi.org/10.1617/s11527-019-1310-8>

### General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [open.access@hw.ac.uk](mailto:open.access@hw.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.

## **Rheology of lime pastes with biopolymer-based additives**

A. Arizzi<sup>a\*</sup>, P.F.G. Banfill<sup>b</sup>

<sup>a</sup> Departamento de Mineralogía y Petrología, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain.

<sup>b</sup> School of Energy, Geosciences, Infrastructure and Society, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

\* Corresponding author (E-mail address: arizzina@ugr.es; Telephone number: +34958243343; ORCID: 0000-0002-8996-0205)

### **Abstract**

The use of industrial limes implies obtaining mortar pastes with worse plasticity and workability compared to lime putties. To overcome this inconvenience, a great number of additives can be used, the majority of them being plasticisers and water-retaining agents. In this work three natural polysaccharides with hydrogel properties (agar-agar, alginate and hyaluronate derivatives) were added to dry-hydrated and natural hydraulic limes to investigate their influence on the rheology of the lime suspensions, as a function of the mixing and dissolving procedures, the additive type and concentration, and the type of lime. Rheological measurements have shown that the yield stress and viscosity of the lime pastes are increased if the additives are pre-mixed with water before adding the lime powder. All additives significantly increase the rheological parameters of the natural hydraulic lime pastes (with a maximum additive concentration of 0.2 g in 1 L of water) but only sodium hyaluronate is effective when mixed with dry hydrated lime. Notwithstanding this, sodium hyaluronate-lime pastes have shown a time-dependent behaviour that must be taken into account during mortar formulation and use. This study lays the foundations for the development of new sustainable lime mortars made with additives derived from natural sources.

**Keywords:** lime; agar-agar; sodium alginate; sodium hyaluronate; plasticity.

### **Acknowledgements:**

This study was financially supported by the European Commission under the Marie Curie program (FP7-PEOPLE-2012-IEF call, research project “NaturaLime”) and by the Spanish program “Juan de la Cierva incorporación” (JDC2015 call, Spanish Ministry of Economy and Competitiveness).

## 1. Introduction

Nowadays additives are essential components of building materials and masons greatly appreciate their use [1]. Nevertheless, their composition, function and characteristics have substantially changed over time since they have had to adapt not only to modern construction techniques but also to the new requirements demanded of industrial mortars. Sugar-based gums and animal glues have been used in the past to improve the workability, waterproofing, mechanical resistance and durability of lime-based mortars [2-4]. Unfortunately, records of the dosages no longer exist and neither are their effects on ancient mortars fully understood. Within the last decade, researchers have investigated the advantages and disadvantages of the use of natural additives in lime-based mortars [5-8].

Different additives can be used depending upon the property of the mortar that needs to be improved. Generally these substances are distinguished according to the moment in the mortar's life at which they must act: when fresh during mixing and application, during drying and hardening, or in its hardened state.

This paper focuses only on specific additives that are useful to increase the workability (intended as viscosity increase) of the pastes made of industrial lime, such as dry hydrated lime and natural hydraulic lime in the form of powder. Lime pastes made with dry hydrated limes are known to be less plastic than lime putties. The plasticity of the latter is given mainly by the fact that the lime particles are thinner and more dispersed [9], giving rise to pastes with higher plastic viscosity [10]. Workability, or plasticity, are in fact closely related to the water-retention capacity of lime and fines, which in turn depends upon the specific surface area and degree of agglomeration of the particles, among other factors [9,10]. Avoiding or reducing particle agglomeration results in an increase in specific surface area and consequently to an increase in mortar viscosity [9]. Particle dispersion also leads to a reduction in the amount of mixing water necessary to achieve optimum consistence and workability. It is known that plasticisers and water-retaining agents prevent particle agglomeration by attaching themselves to the surface of the particles. This causes repulsion among the particles and leads to an improvement in the rheological properties of the mortar [5]. The dispersing properties of a plasticiser depend especially upon the molecular weight and anionic groups of the polymer [11].

With the aim of investigating natural additives to be used for improving the workability of lime pastes, we have studied here three natural polysaccharides (consisting of disaccharide-repeating units), namely *agar-agar*, *alginate* and *hyaluronate* derivatives.

### **1.1 Agar-Agar (AA)**

Agar-agar is a natural polysaccharide extracted from red seaweeds that has been and is still being extensively used in the food and pharmaceutical industries due to its gelling and stabilising properties, as well as exhibiting many biological activities. It is a biopolymer composed of 1,3-linked  $\beta$ -D-galactopyranose (G) and 1,4 linked 3,6-anhydro- $\alpha$ -L-galactopyranose (AG) units, with different possible substituents at various positions in the chain [12]. The agar polymer can be fractioned into two main units: agarose, the neutral fraction with gelling ability, and agarpectin, which contains the charged polysaccharide components. The physical-mechanical and rheological properties of agar vary according to the content of these two units, which in turn depends on the seaweed species the agar was extracted from [13].

At high temperatures, the rheological behaviour of agar sols is similar to dilute solutions of linear polymers (*coil* conformation); whilst at low temperatures below the gelation point ( $T_{gel}$ , the temperature that characterizes the transition from a liquid-like sol to a solid-like gel phase), the behaviour is similar to that of cross-linked polymers [13,14]. Gelation and melting temperatures increase with size of molecules [15] and are normally close to 40 °C and 90 °C, respectively [16].

Both the rheological and the macrostructural properties (related to the microstructure) of an agar gel depend on the preparation procedure adopted (mixing/no mixing; fast mixing/low mixing). Gels mixed at fastest speed are stronger than non-mixed ones or those mixed at lowest speed and this is related to a lower air bubble fraction in the former [16].

### **1.2 Sodium Alginate (AL)**

Due to their hydrogel characteristics (with gelling, film-forming, thickening and stabilizing properties, [17,18]) alginic acid and its derivatives are used in several applications such as food additives, pharmaceuticals, cosmetics and textile manufacturing [19].

Alginate is a natural polysaccharide extracted from brown seaweeds, where it accumulates as “jelly bodies” providing structure and flexibility to the cells of the algae

[20], or produced by bacteria [21]. It is a linear binary co-polymer composed of two units: the (1-4)-linked  $\beta$ -D-mannuronic acid (M) and the  $\alpha$ -L-glucuronic acid (G), which are linked together forming three different types of blocks in the polymer (*M block*, composed of only M-M bonding; *G block*, composed of only G-G bonding; and *M&G random blocks*: composed of M-G random bonding) according to the part of the seaweed used, the harvest location and the harvest season but also to the bacterial origin [22]. Differences in the M/G proportion, distribution and length determine different alginate chemical and physical properties (e.g. G-blocks provide gel forming capacity, MM and MG units provide flexibility, with flexibility increasing in the order GG<MM<MG, (FMC Biopolymer 2013)).

The carboxyl groups of the alginate molecule can react with several cations, producing modifications in the alginate properties. As an example, sodium alginate is soluble in water (it forms a hydrogel) and in alkaline solutions (although the viscosity of sodium alginate decreases in high alkaline system), whilst calcium alginate is insoluble. Alginate has a high affinity towards calcium ions, which are complexed by carboxylate groups in a tetradentate structure (egg-box model).

Alginate hydrogel shows a non-Newtonian (shear-thinning) behaviour [18,23]: the polymer chains align with the flow direction leading to a viscosity decrease. The viscosity of the alginate, however, depends on the polymer concentration and length [20]. At high polymer concentration, the polymer chains are closer and they form a compact network of intermolecular bonding between the non-polar segments that increases viscosity, shear stress and elasticity [24].

According to previous studies on the appropriate mixing and dissolution procedures for the preparation of suspensions of alginates in water, it is recommended to vigorously stir the water while powder is being added. Moreover, pre-mixing with another powder or in a liquid that does not dissolve alginate (such as alcohol, PEG or oil) is known to enhance dispersion and subsequent dissolution [20]. Finally, mixing in a high-speed rotary mixer reduces the quantity of air bubbles in the gel, with respect to that obtained with a hand-mixing technique, thus resulting in greater strength [25].

To our knowledge, adding sodium alginate (0.5%-25% wt. of the material) mixed with agar-agar (in 0.1%-5% wt. of the sodium alginate) in traditional mortars gives rise to “a matrix that is 100% resistant to moisture and mould with superior bond strength, heat resistance, flame retardance, effervescence, unlimited shelf homogeneity with a high degree of flexibility” [26].

### 1.3 Sodium Hyaluronate (HA)

Hyaluronate is a component of the intercellular matrix [27] of most connective tissues, such as bovine and fish vitreous humor, bovine synovial fluid, and it can also be found in the cells of some bacteria [28].

It is a linear polysaccharide composed of two units: glucuronic acid and N-acetyl glucosamine residues, which are linked by  $\beta(1-3)$  and  $\gamma(1-4)$  with each other [29]. The viscoelastic properties shown by this polymer are widely used in dermatological treatments to prevent wrinkles, due to an improvement of the water retention in the skin; in cartilage repair, due to the excellent rheological properties [24]; and in ophthalmic surgery, as promoter of wound healing [29].

The viscosity of hyaluronate is independent of shear rate at low shear rates (Newtonian behaviour over a restricted range of shear rate) but it decreases above a certain shear rate (shear-thinning behaviour) [29]. Studies on the flow properties of the hyaluronic acid in combination with a polyvinyl alcohol in water and borax show that the rheological properties of the suspension increase as the degree of hydrolysis and borax concentration increase [30]. The rheology of hyaluronate is improved when it is chemically modified, by interactions between the macromolecules [27]. Hyaluronate can form bioactive composite coating materials in combination with inorganic phases, such as bioactive glasses and bioceramics (like hydroxyapatite), silica or titania, for application in implants [31].

The hydrogel properties of these bio-polymers support the intention of using them as plasticisers in lime-based pastes and mortars. This paper reports what we believe to be the first attempt to study the rheological properties of mixes of AA/AL/HA and dry-hydrated (CL90S) and natural hydraulic (NHL 3.5) limes, with implications for building material manufacture. In particular, this work aims to study differences in the rheological behaviour of the AA/AL/HA-lime mixes depending on 1) the mixing and dissolving procedures: influence of pre-mixing the additives with lime before adding water and influence of the temperature of mixing water (cold,  $T=18\text{ }^{\circ}\text{C}$ , and warm,  $T=24\text{ }^{\circ}\text{C}$ ); 2) the shear rate; 3) the additive-to-lime proportion (% wt.).

## 2. Materials and methods

### 2.1 Materials

The components used for the preparation of the lime slurries were: aerial (non-hydraulic) dry hydrated lime in the form of dry powder (CL90S, [32]) produced by ANCASA (Seville, Spain); natural hydraulic lime (NHL3.5, [32]) produced by Socli, Italcementi Group; granulated agar-agar (AA), supplied by Merck KGaA; sodium alginate (AL) in the form of fine powder and sodium hyaluronate (HA) in the form of fine powder, both supplied by Shanghai International Co. Ltd.

### 2.2 Experimental work

#### 2.2.1 Empirical observations of the additive-water mixes

To compare the behaviour of AA, AL and HA when mixed with water and to determine the range of concentration (additives:water dosage), dispersions at five different concentrations were prepared to observe differences in their viscosity prior to the rheological measurements. Dispersions were prepared by pouring 0.02, 0.05, 0.1, 0.25 (the latter concentration was used only for AL), 0.5 and 1 g of additives (in the form of powder) into 100 mL of deionised water and stirring them for 180 s under ultrasonic vibration, without heating. The appearance of all dispersions is shown in the Online Resource 1.

*Agar-Agar (AA)*: the powder dissolved in water and formed an opalescent solution with very low viscosity. The dispersion of 1 g of this additive was slightly supersaturated, and some undissolved particles were indeed observed, whilst the 0.02 g dispersion was the clearest one.

*Sodium alginate (AL)*: the powder hardly dissolved in water and formed a yellowish gel whose viscosity increased during the first few minutes. Dispersions made with 1 and 0.5 g were supersaturated, many agglomerates formed and remained undissolved. The 0.02 g dispersion was instead the least viscous and no agglomerates or particles were observed.

*Sodium hyaluronate (HA)*: the powder dissolved better than AL in water but still some whitish agglomerates were observed in the 1 g and 0.5 g dispersions. Dispersions of this material were transparent and clear, with the 0.02-0.05 g dispersions being the clearest. The pH of the water mixes prepared mixing 0.1g of additives in 100 mL of deionised water was 9.3 for both AA and AL and 9.0 for HA.

### 2.2.2 Rheological measurements on lime pastes

A total of 70 different mixes were prepared for the rheological study of the lime and lime-additives pastes, which was carried out by means of a CSL500<sup>2</sup> rheometer (TA Instruments) using an interrupted helical impeller (28mm diameter) in a smooth cylinder (30mm diameter) [33], using the following experimental stages, with no time gap between each stage.

- 1) *Pre-shear*: PS1, 50/s in 60s; PS2, 100/s in 60s; and PS3, 200/s in 60s.
- 2) *Equilibrium*: 15s unsheared.
- 3) *Ramp up-1*: from 0 to 10/s in 20 steps over 60s.
- 4) *Ramp up-2*: from 10 to 200/s in 20 steps over 60s.
- 5) *Ramp down*: from 200 to 0/s in 20 steps over 60s.

The shear rates quoted are average effective values obtained from a prior calibration of the impeller using the procedure developed by Gill and Banfill [34] from that of Tattersall and Banfill [35]. Six trials of the procedure were performed in water and oil, with and without water bath, before testing the suspensions.

The variable parameters studied were:

1. Mixing procedures:
  - a) *Additive to lime paste*: Pre-mix of lime with water (T=18 °C) and subsequent addition of additive powder
  - b) *Powders to water*: Pre-mix of additives and lime in powder and subsequent addition of water (T=18 °C)
  - c) *Additive paste (cold) to lime*: Pre-mix of additives with water (T=18 °C) and subsequent addition of lime powder
  - d) *Additive paste (warm) to lime*: Pre-mix of additives with warm water (T=24 °C) and subsequent addition of lime powder. Using warm water aimed at increasing the dissolution of the additive in water. This mixing procedure was not considered for Agar-Agar (AA) because this additive already dissolves at T=15 °C (no changes in rheology are expected at water temperatures higher than 15 °C). Moreover, if AA dissolves at 15 °C, this means that it is already dissolved at 18 °C, temperature of the tap water used for the preparation of mortars in mixing procedures 1 to 3.
2. Lime pastes:

- Dispersions of CL90S in water, water:lime dosages by weight: 1.2:1; 1.3:1; 1.4:1; 1.5:1 (equivalent to 0.6:1; 0.65:1; 0.7:1; 0.75:1 by volume). These dosages were chosen on the basis of subjective observations (“a bit stiff”, “plastic”, “a bit plastic”, “a bit liquid”) made on different lime-water mixes (from 1.2:1 to 2:1 water:lime dosage).
  - Dispersions of NHL3.5 in water, water:lime dosages by weight: 0.6:1; 0.7:1; 0.8:1; 0.9:1 (equivalent to 0.44:1; 0.52:1; 0.59:1; 0.67:1 by volume). These dosages were likewise chosen on the basis of subjective observations (“a bit stiff”, “plastic”, “a bit plastic”, “a bit liquid”) made on different mixes (from 0.5:1 to 2:1 water:lime dosage).
  - Dispersions of the additives in water: 0.2, 0.35, 0.5 g in 1 L water for AA and AL and 0.06, 0.2 and 0.35 g in 1L water for HA. These concentrations were established on the basis of the subjective observations described above.
3. Mixing speed:
- Different pre-shear rates were used only on HA suspensions: 50/s, 100/s, 200/s in 60s. All the other tests were performed at a pre-shear rate of 50/s in 60s.

### **2.2.3 Analysis of variance (ANOVA)**

A complete factorial experiment in which every combination of additive type A, concentration C (0.2, 0.35 and 0.5g/1L of water) and mixing procedure M (additive to lime paste, powders to water and additive paste (cold) to lime) was tested for both agar-agar and sodium alginate, in both CL90S and NHL3.5 pastes at 1.3:1 and 0.7:1 respectively, enabled the significance of the main factors and interactions to be assessed using Analysis of Variance (ANOVA) [36,37]. Not every combination could be tested for sodium hyaluronate but conclusions can be inferred for that additive by assuming that the same experimental error terms are applicable.

## **3. Results of the rheological measurements**

### **3.1 Flow curves of lime pastes**

The flow curves of the suspensions of CL90S and NHL3.5 in water prepared with 4 different water:lime dosages (CL90S: 1.2:1; 1.3:1; 1.4:1; 1.5:1 and NHL3.5: 0.6:1; 0.7:1; 0.8:1; 0.9:1 by weight) are given in the Online Resource 2, showing the quality of the fit to the Modified Bingham equation,  $\sigma = \sigma_y + \mu\dot{\gamma} + c\dot{\gamma}^2$  [38] where a negative

value of  $c/\mu$  denotes shear thinning and a positive value denotes shear thickening. Noting the significant structural breakdown exhibited by the hysteresis loops in the stiffest paste in each series, it was finally decided to use suspensions of the lime with the additives at a water:lime ratio of 1.3:1 for CL90S and of 0.7:1 for NHL3.5. The experimental error was estimated from the ANOVA, as discussed in detail later. Fig. 1-3 show examples of the flow curves obtained with pastes containing additives. The outlying points visible on certain flow curves in Fig. 1-3 seem to be artefacts of the data acquisition system and were removed before curve fitting was carried out.

Tables 1 and 2 summarise the rheological parameters obtained by fitting the experimental flow curves to the Modified Bingham equation.

### 3.2 Analysis of variance (ANOVA) on the rheological parameters

ANOVA [37] was carried out using each measured value (yield stress, plastic viscosity, constant  $c$  and ratio of  $c/\mu$ ) for both CL90S and NHL3.5 pastes. The overall variation (total sum of squares) is partitioned among the main effects (factors A, C and M) and the interactions (AC, AM and CM). The three-factor interaction (ACM) was taken as the residual and in an unreplicated experiment can be used as an initial estimate of the error variance [36]. The mathematical model for the experimental value  $x_{ijk}$  is:

$$x_{ijk} = X + A_i + C_j + M_k + (A \times C)_{ij} + (A \times M)_{ik} + (C \times M)_{jk} + \varepsilon_{ijk}$$

where  $X$  is the overall average,  $A_i$  is the effect of A at the  $i$ th level,  $C_j$  is the effect of C at the  $j$ th level,  $M_k$  is the effect of M at the  $k$ th level.  $(A \times C)_{ij}$  etc denotes the joint effect of A at the  $i$ th level and C at the  $j$ th level, i.e. the interaction effect.  $\varepsilon_{ijk}$  is random error.

Tables 3-6 show the results of the ANOVA for each measured parameter: F-ratios greater than those needed for significance at the 5% level are marked with a double asterisk\*\*.

The ANOVA shows that for CL90S pastes no factors have a significant effect on yield stress, plastic viscosity or coefficient  $c$ , and only the interactions AC and CM are significant for  $c/\mu$ . For NHL3.5 pastes the only significant effect is of mixing on yield stress, although additive is close to being significant for plastic viscosity. Since none of the interaction terms are significant for yield stress, plastic viscosity or coefficient  $c$ , they can be combined to give a better estimate of experimental error (i.e. one based on more degrees of freedom) [36]. Testing the main effects (A, C and M) against this new residual (made up of interactions AC, AM, CM and ACM and totalling 12 degrees of

freedom) shows that for CL90S pastes additive A has a significant effect on yield stress, whilst for NHL3.5 pastes mixing M has a significant effect on yield stress and plastic viscosity and additive A has a significant effect on plastic viscosity. No other effects are significant but the effects on  $c/\mu$  of CL90S pastes were not analysed in this way because of the significant AC and CM interactions noted above. Lumping the interaction terms in this way gives an estimate of the error mean square for 12 degrees of freedom and hence the RMS error, from which 90% confidence intervals can be calculated as shown in Table 7.

Whilst it was not possible to perform two replicates of the entire experiment (which would have involved considerably more tests), a single paste was replicated five times to check these confidence intervals. CL13 (table 1) gave extrapolated yield stresses of 14.75, 17.39, 17.14\*, 23.81\*, 30.70\* but the asterisked values are derived from flow curve measurements with very low values of  $R^2$ . However, the difference between 14.75 and 17.39 is 2.64, which is less than twice the CI. Likewise, for the plastic viscosities of 0.275, 0.251, 0.04\*, 0.22\*, 0.36\* the difference between the two reliable values is 0.024, which is less than twice the CI. The values of constant  $c$  and of  $c/\mu$  are also less than twice the CI. All this confirms that the confidence intervals given in table 7 are consistent with the replicated tests. Finally, it can be noted that the tests on CL90S pastes have greater CIs than those on NHL3.5 pastes so it might be considered reasonable to guess that the CI of the  $c/\mu$  for the CL90S pastes, which could not be determined directly from the ANOVA, is  $2 \times 10^{-6}$ .

Finally, the least significant difference (LSD) is given by  $s \sqrt{(2/n_i) t_{0.05,ne}}$ , where  $s$  is the square root of the residual mean square,  $n_i$  is the number of values at each level of the factor being considered and  $ne$  is the number of degrees of freedom used in calculating the residual mean square (in this case 12) [37]. Considering yield stress, for factor A the LSD is 2.50 whilst for factors C and M the LSD is 3.06. These LSDs are about twice the 90% CIs given in table 7, so as a practical test it can be concluded that any difference between two measurements that is more than twice the relevant CI can be taken as significant.

### **3.3 Effect of the mixing procedure and additive type on yield stress and plastic viscosity**

Table 8 summarises, from the raw data in tables 1 and 2, the effect of mixing procedure (as defined in section 2.2.2) on yield stress and plastic viscosity of pastes containing

agar-agar (AA) and sodium alginate (AL). There is no difference between procedures a, adding the additive to the lime paste, and b, adding the powders to water, but procedure c, adding the cold additive paste to lime, consistently increases the yield stress. For sodium hyaluronate (HA) there is an effect of mixing procedure only at 0.06 g/L in CL90S pastes: procedure b gives the lowest yield stress, c an intermediate value and a gives the highest yield stress. There is no effect of mixing procedure at the higher concentrations. In the only measurable NHL3.5 pastes (at 0.2 g/L HA) procedures a and b are indistinguishable but c gives the lowest yield stress.

In the case of plastic viscosity the procedures are indistinguishable in CL90S pastes, and in NHL3.5 pastes only procedure c (adding cold additive paste to lime) consistently increases plastic viscosity compared to a and b. For HA in CL90S pastes there is an effect of mixing procedure only at 0.2 g/L, where procedure b gives a significantly higher plastic viscosity than a and c. In the only measurable NHL3.5 paste procedures b and c are indistinguishable but a gives the lowest plastic viscosity.

Table 9 summarises, from the raw data in tables 1 and 2, the effect of additive type on the yield stress and plastic viscosity of CL90S and NHL3.5 pastes, averaged over the different mixing procedures. It should be noted that only three results of HA-containing pastes contribute to table 9 because the higher concentrations of HA required increases in the water:lime ratio, as shown in tables 1 and 2, thus precluding direct comparison. The relevant pastes are CLHA0613: 0.06g HA/1L water and water:lime ratio of 1.3:1, and NHL0607: 0.06g HA/1L water and water:lime ratio of 0.7:1.

Table 10 shows the dramatic effect of HA on CL90S and NHL3.5 pastes: it significantly increases yield stress in CL90S paste and both yield stress and plastic viscosity in NHL3.5 pastes, but there is no difference between the mixing methods.

### **3.4 Pre-shear and time dependence of lime pastes with sodium hyaluronate**

The observed effect of HA suggested that structural breakdown might be important and the influence of shear history and resting time was investigated in more detail. CL90S pastes at 1.3:1 water:lime ratio containing HA at 0.06g/L prepared with mixing procedure a (additive to lime paste) were tested with three different pre-shear rates: 50, 100 and 200/s. Table 11 shows that yield stress and plastic viscosity decrease significantly, but not  $c$  or  $c/\mu$ . Additionally the hysteresis loop in the flow curve observed at 50/s shrank at 100/s and was absent at 200/s, giving superimposable up and

down curves. These effects are consistent with the occurrence of structural breakdown and suggest that the HA creates a shear sensitive structure in CL pastes.

CL90S pastes prepared in the same way were then presheared at 100/s and allowed to stand before testing after 5 (mixing procedure a), 10 and 15 minutes. Table 11 also shows that CL90S lime pastes stiffen significantly (but transiently) at 10 minutes.

To test whether HA is alkali sensitive the pH was monitored during the first 15 minutes of both the lime pastes alone and the pastes with HA. Interestingly, the pH of both CL90S and NHL3.5 pastes does not change over the first 15 minutes (the value is  $12.6 < \text{pH} < 12.8$ ), and the addition of HA does not induce any change in the pH either (pH of HA in water  $\sim 9$ ). Therefore, it is possible that  $\text{Ca}^{2+}$  ions could be complexed by the carboxylate groups of the HA molecules, forming a tetradentate structure (the egg-box model), and releasing  $\text{Na}^+$  ions [39]. Calcium hyaluronate is insoluble in alkali so the stiffening between 5 and 10 minutes after mixing could occur because  $\text{Ca}(\text{OH})_2$  from the lime dissolves in water and the  $\text{Ca}^{2+}$  ions are complexed by the hyaluronate. If the tetradentate  $\text{Ca}^{2+}$  ions were to form bridges between hyaluronate molecules this would stiffen the paste, as observed. In a pharmaceutical application of HA, Bolshakova et al [40]. reported that sodium hyaluronate was adsorbed on a  $\text{CaCO}_3$  surface through chemisorption with formation of calcium hyaluronate and its subsequent destruction over time. This suggests that the calcium hyaluronate formed in a lime paste is short-lived and potentially explains the transient increase in yield stress and plastic viscosity in Table 11.

#### **4. Discussion and conclusions**

According to the least significant differences mentioned above, pre-mixing the additive with water before adding the lime (both CL90S and NHL3.5) (*mixing procedures c and d*) gives higher values of yield stress in agar-agar and sodium alginate suspensions (Tables 1 and 2) in comparison with the addition of these additives to the lime paste or the lime powder (*mixing procedure a and b*). This effect is slightly more significant for the alginate. Moreover, there is a further increase in the shear stress when the additive is mixed with warm water (*mixing procedure d*, Tables 1 and 2).

The effect of mixing procedure is not as clear for the pastes with sodium hyaluronate, as the trend changes depending on the water:lime ratio and additive dosage.

Agar-agar and sodium alginate increase the yield stress and plastic viscosity of all pastes but the slight effect on CL90S pastes is not significant. Sodium hyaluronate significantly increases both parameters for CL90S paste and all three additives significantly increase yield stress and plastic viscosity of NHL3.5 pastes. In terms of the concentration of the various additives, 0.2g/L of agar-agar and sodium alginate is sufficient to significantly increase the yield stress and plastic viscosity of NHL3.5 paste, but there is no further significant change at 0.35 and 0.5g/L. It would be useful to investigate lower concentrations to establish if there is a threshold concentration for these additives to be used in practice.

The time-dependent behaviour of pastes containing sodium hyaluronate suggests that, whilst this additive is likely to have beneficial effects on the performance of lime-based materials, care must be taken in their formulation and use in order to ensure that appropriate working properties are maintained in use. Complexation tests should be carried out in the future in order to prove the influence of  $\text{Ca}^{2+}$  ion complexation on the rheological performances of sodium hyaluronate mixed with lime.

This study has demonstrated that the gelling properties of some natural additives can be used to improve the plasticity of pastes made with industrial limes, thus allowing to approach the workability of lime putties, as long as the right additive concentration and mixing procedure are chosen. No more than 0.2 g of additive per litre of water are needed to obtain an increase in the viscosity of the lime pastes and the use of tap water with a temperature ranging from 18 to 24 °C would help improving the dissolution of the additives in water before adding the lime. However, the rheological data show that the effect of the three additives is more pronounced when they are mixed with natural hydraulic lime (NHL pastes). In the practice, the use of natural additives such as those studied here can be taken into account for the design of more workable and sustainable natural hydraulic lime mortars.

Further studies on the lime hardening in the presence of these natural polysaccharides will be essential for corroborating their viability as additives in lime mortars.

## **References**

- [1] Hendrickx R (2009) The adequate measurement of the workability of masonry mortar. PhD Thesis, Katholieke Universiteit of Leuven, Belgium.
- [2] Sickels LB (1981) Organic additives in mortars. Edinburgh Architecture Research 8:7-20.

- [3] Garate Rojas E (1993) *Las Artes de la Cal*. CBRIC-MEC, Madrid.
- [4] Cowper AD (1927) *Lime and Lime mortars*. Donhead Ed. Reprinted in 1998 by Building Research Establishment Ltd.
- [5] Seabra MP, Paiva H, Labrincha JA, Ferreira VM (2009) *Constr Build Mater* 23:1147-1153.
- [6] Izaguirre A, Lanas J, Alvarez JI (2011) Characterization of aerial lime-based mortars modified by the addition of two different water-retaining agents. *Cem Concr Compos* 33:309-318.
- [7] Ventolá L, Vendrell M, Giraldez P, Merino L (2011) Traditional organic additives improve lime mortars: New old materials for restoration and building natural stone fabrics. *Constr Build Mater* 25:3313-3318.
- [8] Rodríguez-Navarro C, Ruiz-Agudo E, Burgos-Cara A, Elert K, Hansen EF (2017) Crystallization and colloidal stabilization of  $\text{Ca}(\text{OH})_2$  in the presence of nopal juice (*Opuntia ficus indica*): implications in architectural heritage conservation. *Langmuir*, 33(41):10936-10950.
- [9] Rodríguez-Navarro C, Ruiz Agudo E, Ortega-Huertas M, Hansen E (2005) Nanostructure and Irreversible Colloidal Behavior of  $\text{Ca}(\text{OH})_2$ : Implications in Cultural Heritage Conservation. *Langmuir*, 21:24.
- [10] Ruiz-Agudo E, Rodríguez-Navarro C (2010) Microstructure and Rheology of Lime Putty. *Langmuir* 26(6):3868–3877.
- [11] Vieira MC, Klemm D, Einfeldt L, Albrecht G (2005) Dispersing agents for cement based on modified polysaccharides. *Cem Concr Res* 35:883-890.
- [12] Francavilla M, Pineda A, Lin CSK, Franchi M, Trotta P, Romero AA, Luque R (2013) Natural porous agar materials from macroalgae. *Carbohydr Polym* 92:1555-1560.
- [13] Labropoulos KC, Niesz DE, Danforth SC, Kevrekidis PG (2002a) Dynamic rheology of agar gels: theory and experiments. Part I. Development of a rheological model. *Carbohydr Polym* 50:393-406.
- [14] Labropoulos KC, Niesz DE, Danforth SC, Kevrekidis PG (2002b) Dynamic rheology of agar gels: theory and experiments. Part II: gelation behaviour of agar sols and fitting of a theoretical rheological model. *Carbohydr Polym* 50:393-406.
- [15] Lahrech KH, Safouane A, Peyrelasse J (2005) Sol state formation and melting of agar gels rheological study. *Physica A* 358:205-211.

- [16] Ross KA, Pyrak-Nolte LJ, Campanella OH (2006) The effect of mixing conditions on the material properties of an agar gel-microstructural and macrostructural considerations. *Food Hydrocolloid* 20:79-87.
- [17] Park H, Lee KY (2011) Alginate /hyaluronate hydrogels for cartilage regeneration. *J Control Release* 152:e192-e269.
- [18] Morais DS, Rodrigues MA, Silva TI, Lopes MA, Santos M, Santos JD, Botelho CM (2013) Development and characterization of novel alginate-based hydrogels as vehicles for bone substitutes. *Carbohydr Polym* 95:134– 142.
- [19] Kimica web page, consulted online on 21 Nov 2013: [http://www.kimica-alginate.com/alginate/chemical\\_structure.html](http://www.kimica-alginate.com/alginate/chemical_structure.html).
- [20] FMC BioPolymer. The science of formulation. Alginates. Accessed 21 Nov 2013: [www.fmcbiopolymer.com/portals/pharm/content/docs/alginates.pdf](http://www.fmcbiopolymer.com/portals/pharm/content/docs/alginates.pdf).
- [21] Andersen T, Strand BL, Formo K, Alsberg E, Christensen BE (2012) Alginates as biomaterials in tissue engineering. *J Carbohydr Chem* 37:227—258.
- [22] Oerther S, Le Gall H, Payan E, Lopicque F, Presle N, Hubert P, Dexheimer J, Netter P, Lopicque F (1999) Hyaluronate-alginate Gel as a Novel Biomaterial: Mechanical Properties and Formation Mechanism. *Biotechnol Bioeng* 63(2):206-215.
- [23] Storz H, Zimmermann U, Zimmermann H, Kulicke WM (2010) Viscoelastic properties of ultra-high viscosity alginates. *Rheol Acta* 49:155–167.
- [24] Pelletier S, Hubert P, Payan E, Marchal P, Choplin L, Dellacherie E (2001) Amphiphilic derivatives of sodium alginate and hyaluronate for cartilage repair: Rheological properties. *J Biomed Mater Res* 54:102–108.
- [25] Inoue K, Song YX, Kamiunten O, Oku J, Terao T, Fujii K (2002) Effect of mixing method on rheological properties of alginate impression materials. *J Oral Rehabil* 29:615-619.
- [26] US8246733B2 patent (2009) Inventor: Daniel R. DeBrouse. Original Assignee: Tamarisk Tech LLC.
- [27] Charlot A, Auzely-Velty R (2007) Novel Hyaluronic Acid Based Supramolecular Assemblies Stabilized by Multivalent Specific Interactions: Rheological Behavior in Aqueous Solution. *Macromolecules* 40:9555-9563.
- [28] Murado MA, Montemayor MI, Cabo ML, Vázquez JA, González MP (2012) Optimization of extraction and purification process of hyaluronic acid from fish eyeball. *Food and Bioproducts Processing* 90:491–498.

- [29] Mo Y, Takaya T, Nishinari K, Kubota K, Okamoto A (1999) Effects of Sodium Chloride, Guanidine Hydrochloride, and Sucrose on the Viscoelastic Properties of Sodium Hyaluronate Solutions. *Biopolymers* 50:23–34.
- [30] Park HO, Hong JS, Ahn KH, Lee SJ, Lee SJ (2005) Influence of preparation parameters on rheological behavior and microstructure of aqueous mixtures of hyaluronic acid/poly(vinyl alcohol). *Korea-Aust Rheol J* 17(2):79-85.
- [31] Seuss S, Boccaccini AR (2013) Electrophoretic Deposition of Biological Macromolecules, Drugs and Cells. *Biomacromolecules* 14:3355–3369
- [32] EN 459-1 (2010) Building Lime. Part 1: Definitions, specifications and conformity criteria. CEN, European Standard.
- [33] Banfill P, Frias M (2007) Rheology and conduction calorimetry of cement modified with calcined paper sludge. *Cem Concr Res* 37:184-190
- [34] Gill SM, Banfill PFG (1987) The viscometric examination of cement pastes with interrupted helical impellers. *Adv Cem Res* 1:92-98.
- [35] Tattersall GH, Banfill PFG (1983) *The rheology of fresh concrete*. Pitman, London.
- [36] Davies OL (1957) *The design and analysis of industrial experiments*. London: Oliver and Boyd.
- [37] Chatfield C (1983) *Statistics for technology: a course in applied statistics*. Third Edition (revised). Ed. Chapman & Hall, US, ISBN: 9780412253409
- [38] Yahia A, Khayat KH (2001) Analytical models for estimating yield stress or high performance pseudoplastic grout. *Cem Concr Res* 31:731-738.
- [39] Choi JH, Kim SO, Linardy E, Dreaden EC, Zhdanov VP, Hammond PT, Cho NJ (2015) Adsorption of hyaluronic acid on solid supports: role of pH and surface chemistry in thin film self-assembly. *J Colloid Interf Sci*, 448:197-207.
- [40] Bolshakova AE, Melnikova NB, Nistratova LN, Pyanzina IP, Salikova TV, Gavrilova SA, Krasilnikova EV (2012) Suspension based on calcium carbonate and sodium hyaluronate for the prevention and treatment of bone diseases. *Pharm Chem J*, 46(7):449-455.

### **Figures captions**

**Figure 1.** Flow curves (shear rate,  $\dot{\gamma}$  ( $s^{-1}$ ), versus shear stress,  $\sigma$  (Pa)) of CL90S and NHL3.5 pastes containing agar-agar at 0.2 g/L. The codes in the legend are the corresponding suspension names given in Tables 1 and 2.

**Figure 2.** Flow curves (shear rate,  $\dot{\gamma}$  ( $s^{-1}$ ), versus shear stress,  $\sigma$  (Pa)) of CL90S and NHL3.5 pastes containing sodium alginate at 0.2 g/L. The codes in the legend are the corresponding suspension names given in Tables 1 and 2.

**Figure 3.** Flow curves (shear rate,  $\dot{\gamma}$  ( $s^{-1}$ ), versus shear stress,  $\sigma$  (Pa)) of CL90S and NHL3.5 pastes containing sodium hyaluronate at 0.2 g/L. The codes in the legend are the corresponding suspension names given in Tables 1 and 2.

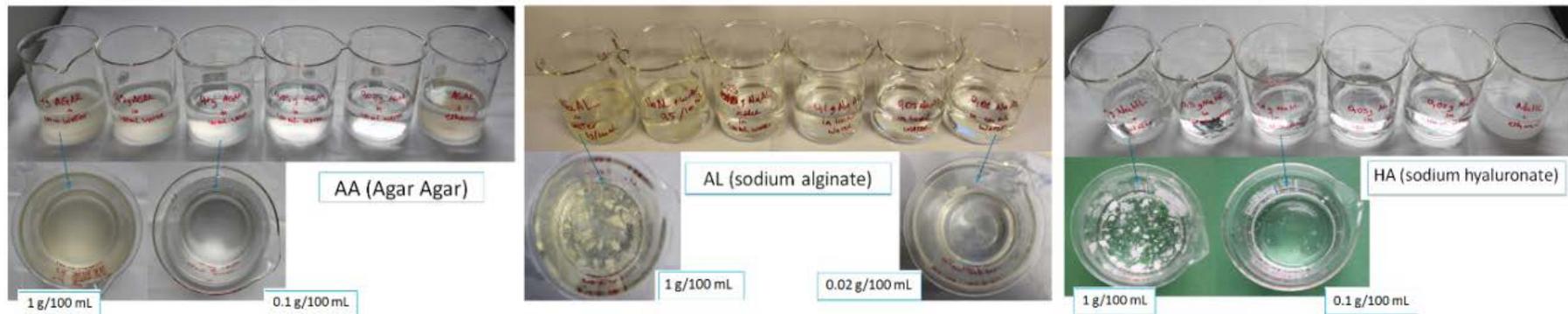
## Rheology of lime pastes with biopolymer-based additives

A. Arizzi<sup>a\*</sup>, P.F.G. Banfill<sup>b</sup>

<sup>a</sup> Departamento de Mineralogía y Petrología, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain.

<sup>b</sup> School of Energy, Geosciences, Infrastructure and Society, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

\* Corresponding author (E-mail address: arizzina@ugr.es; Telephone number: +34958243343; ORCID: 0000-0002-8996-0205)



**Online Resource 1.** Dispersions of AA, AL and HA at different concentrations in water.

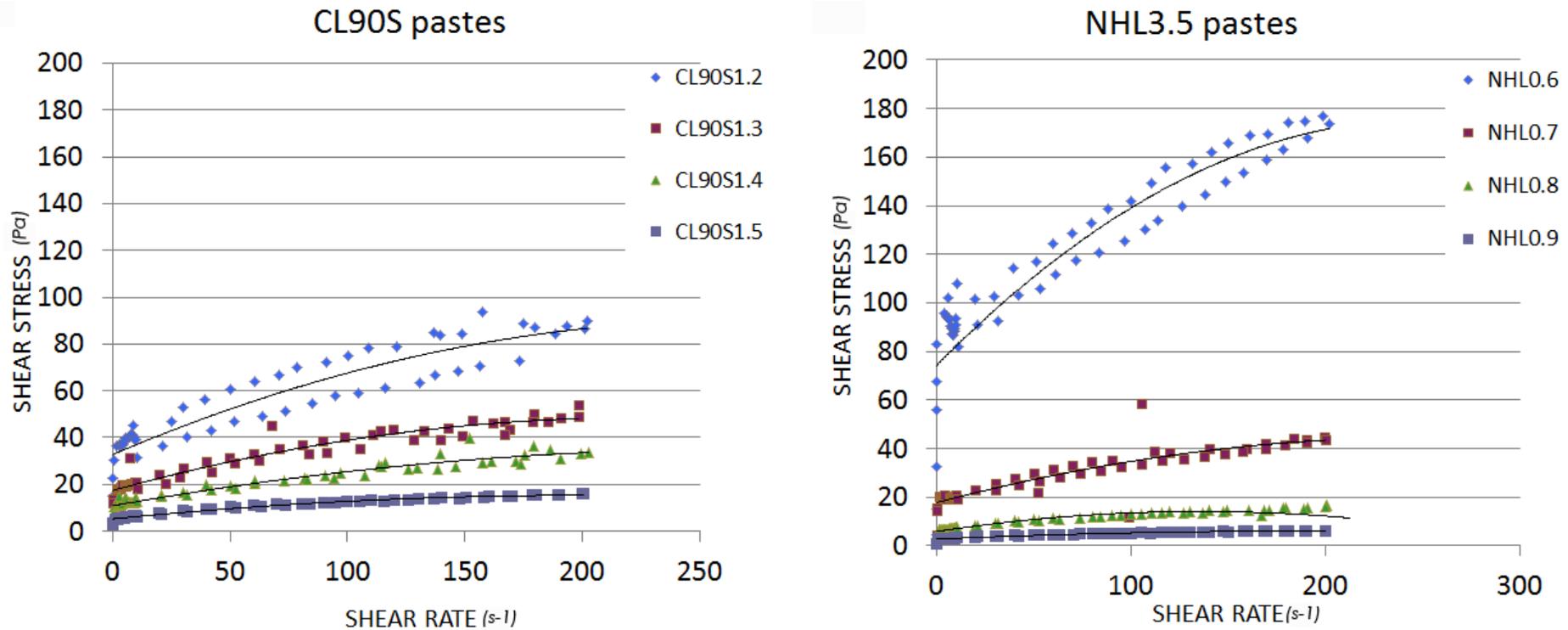
## Rheology of lime pastes with biopolymer-based additives

A. Arizzi<sup>a\*</sup>, P.F.G. Banfill<sup>b</sup>

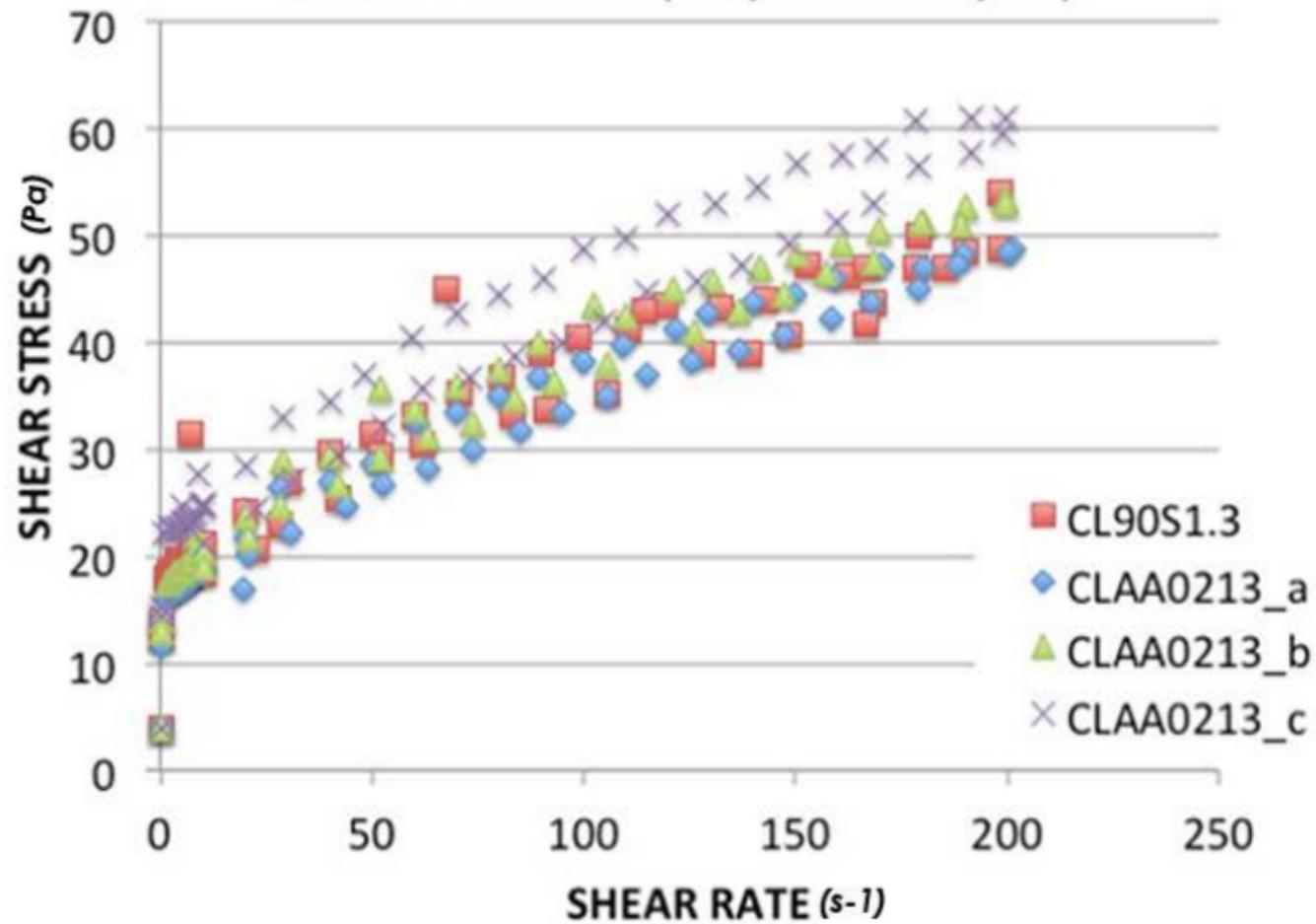
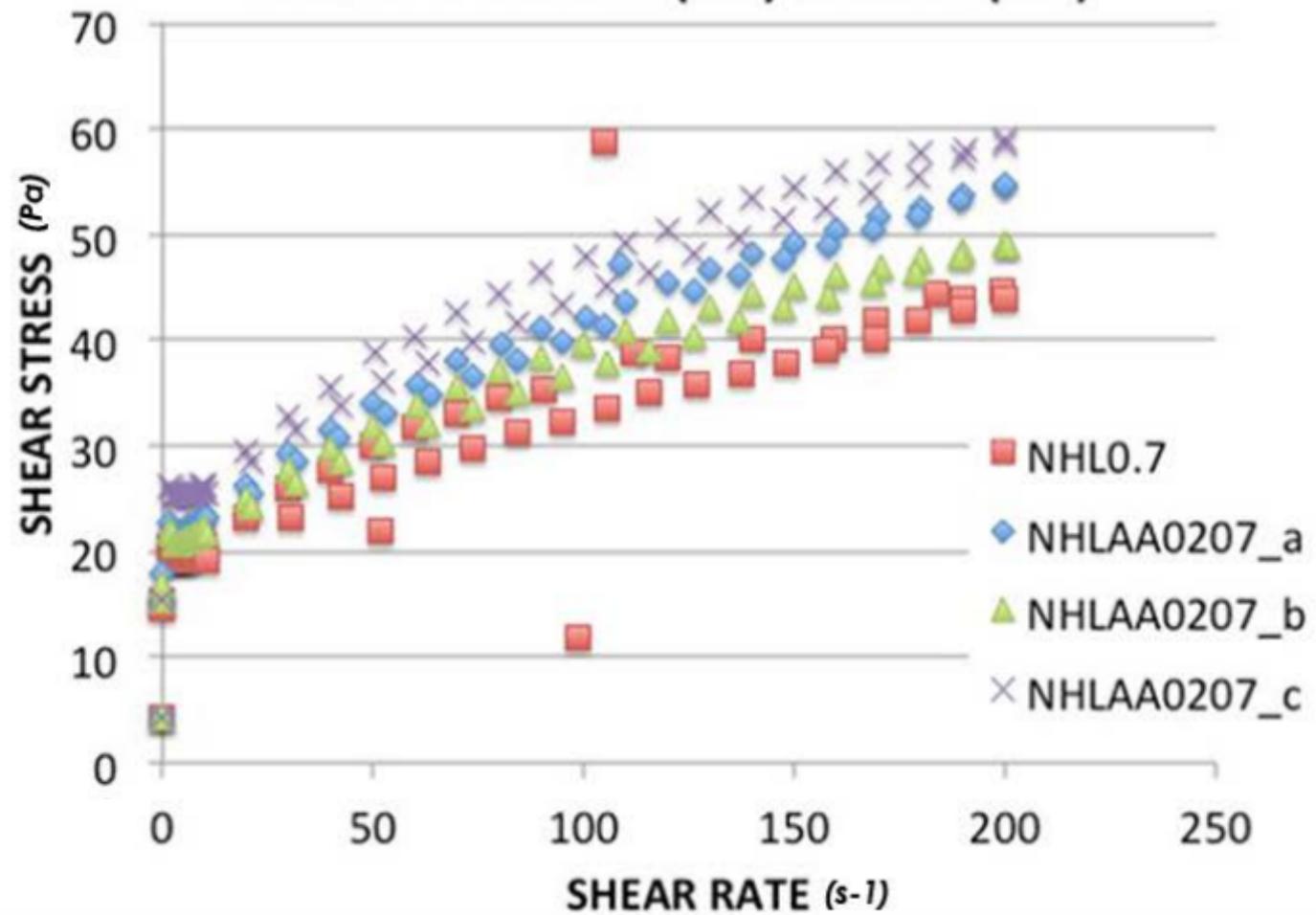
<sup>a</sup> Departamento de Mineralogía y Petrología, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain.

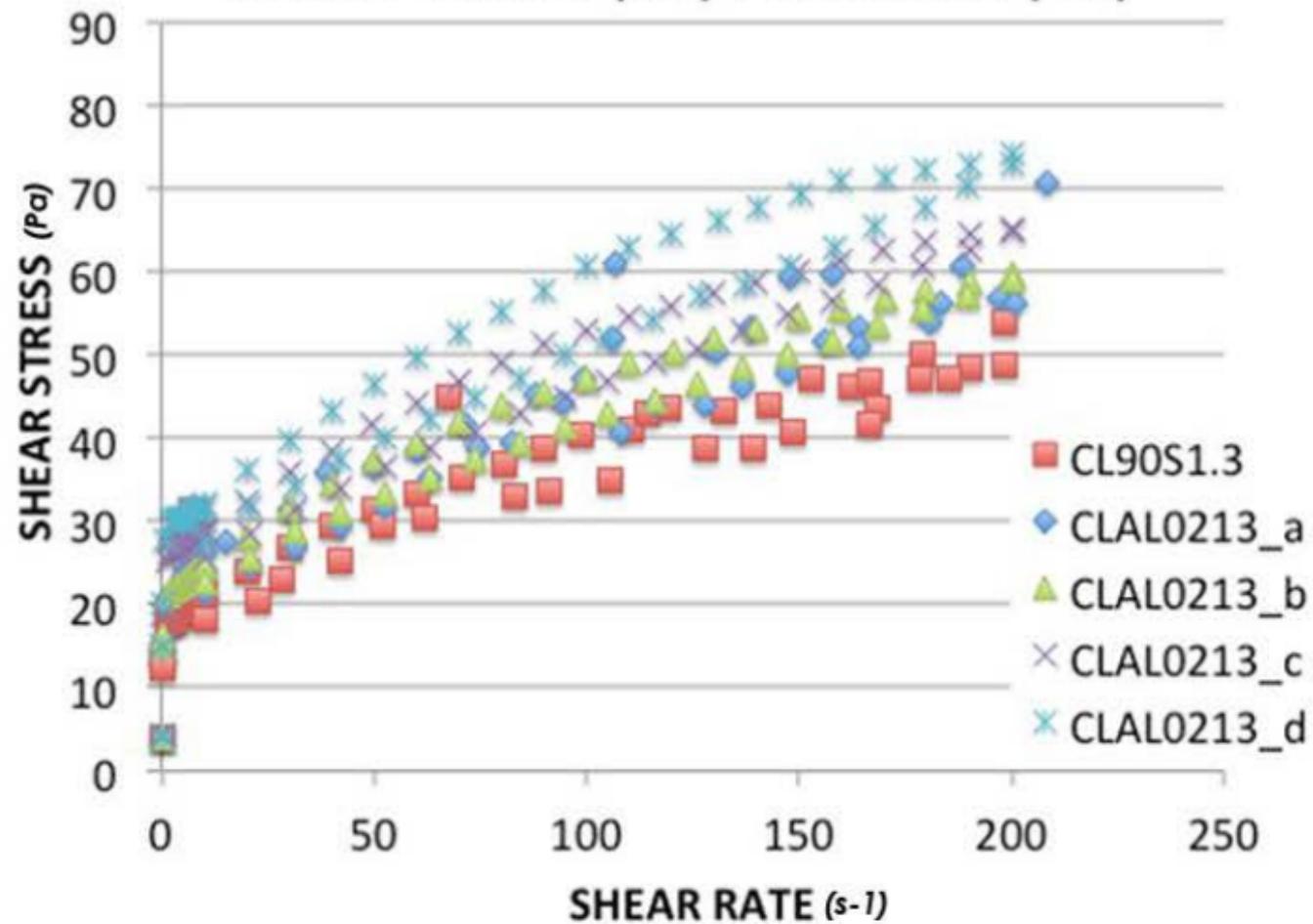
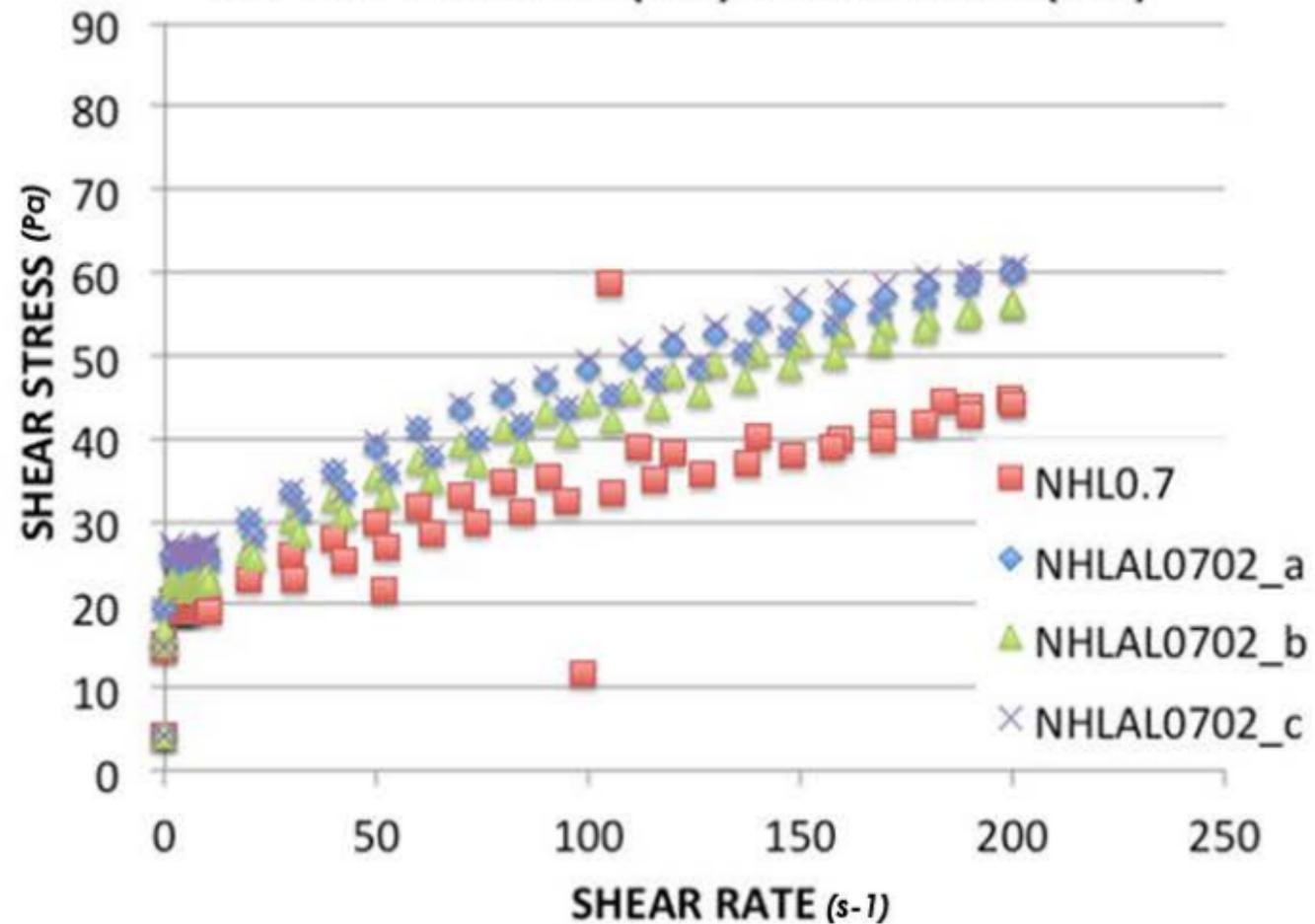
<sup>b</sup> School of Energy, Geosciences, Infrastructure and Society, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

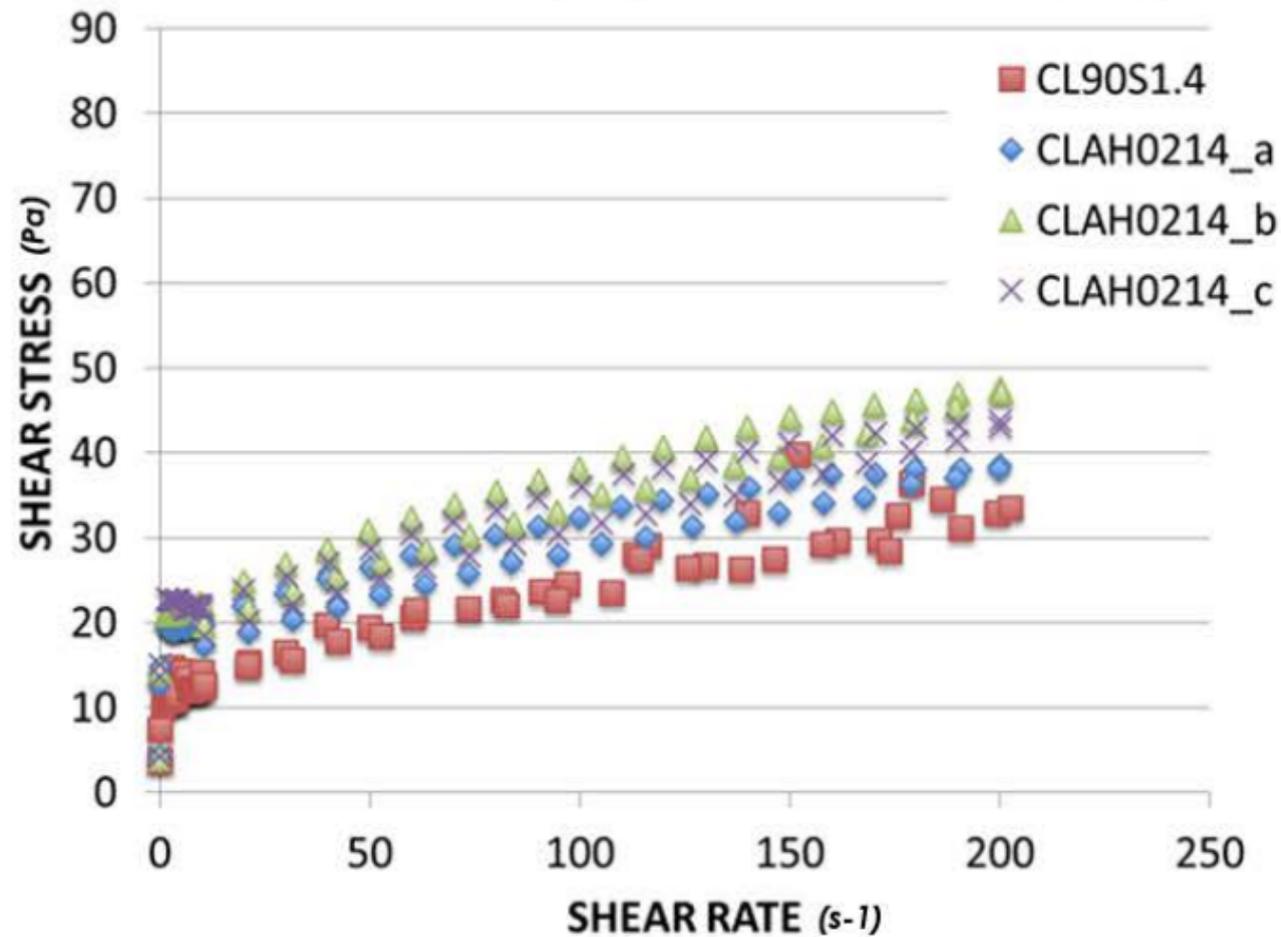
\* Corresponding author (E-mail address: arizzina@ugr.es; Telephone number: +34958243343; ORCID: 0000-0002-8996-0205)



**Online Resource 2.** Flow curves (shear rate,  $\dot{\gamma}$  (s<sup>-1</sup>), versus shear stress,  $\sigma$  (Pa)) of CL90S and NHL3.5 pastes at different water:lime dosages.

**CL90S + WATER (1.3) + AGAR (0.2)****NHL3.5 + WATER (0.7) + AGAR (0.2)**

**CL90S + WATER (1.3) + ALGINATE (0.2)****NHL3.5 + WATER (0.7) + ALGINATE (0.2)**

**CL90S + WATER (1.4) + HYALURONATE (0.2)****NHL3.5 + WATER (0.8) + HYALURONATE (0.2)**