

Are Alkali Activated binder behaviors intermediate between cement and mineral suspensions?

Teresa Liberto¹, Maurizio Bellotto², Agathe Robisson³

^{1,3} Vienna University of Technology, Faculty of Civil Engineering, Research Area Building Materials, Materials Technology E207-01

² Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering G.Natta, Milano, Italy

Abstract

In this work, we compare rheological oscillation measurements on concentrated suspensions of Ordinary Portland Cement (OPC), alkali activated binder (AAB) and calcite. For the three systems, a range of volume concentrations is defined in which these dense suspensions show an “attractive gel-like behavior” [1-3]. The amplitude of this concentration range depends on the extension length of the interparticle forces, and on their nature. We characterize and compare the elastic domains, dominated by the interaction forces, extracting the fractal dimensions of the flocs formed upon self-assembly of the primary particles. We thus provide a hint on the gel heterogeneities and on the deformation mechanisms [1-3]. This preliminary work aims at being a baseline to better understand the nature of the interactions between cement or AAB particles, leading to differences in the fresh state behaviour and setting times, by analyzing the macroscopic rheological response [4]. This innovative approach, obtained from applying a classic fractal model [1], was successfully used to characterize calcite paste [3,4]. The ultimate goal is to control the interaction forces through the fine-tuning of the solid-liquid equilibria, in order to adjust the properties of the paste and fulfill the specific requirements of the final application.

1 Introduction

Alkali-activated binders have been widely discussed and promoted as an essential component of the current and future toolkit of ‘sustainable cementing binder systems’ [5]. However, when selecting a binder alternative to OPC, it is necessary to take into account several aspects beyond the mere mechanical performances and durability properties. First of all, if the binder is used to produce a ready-mixed concrete, it is advisable to use a “one part” material which sets and hardens upon contact with water only, so that the available mixing and processing technologies can be used [6]. Also, with regards to the life-cycle assessment (LCA), the impact of the activating system needs to be duly included. In the case of sodium hydroxide or sodium silicate activation, the LCA will be negatively and significantly impacted [7]. Finally, the fresh-state properties, the response to the addition of superplasticizers and the cohesivity and pumpability of AAB may widely differ from OPC. These requirements are sometimes conflicting with regards to the choice of the AAB system. In the following study, we selected a well-known and long-time used AAB constituted by ground and granulated blast-furnace slag (GGBS) activated with sodium carbonate (or sodium sulphate) [8]. A number of buildings erected with such a binder in the 1950s show little signs of degradation apart from carbonation and are still having compression strength higher than the design values [9]. This binder also has a low environmental footprint, good resistance to environmental attack and it is aesthetically alike to white cement. It is however less cohesive than OPC and does not respond properly to the addition of superplasticizers [10].

The control of cohesivity and the adsorption of superplasticizer are regulated by the surface charge density, surface potential, the ionic composition and ionic force of the interstitial solution [11]. In this study, we measure and compare the rheological properties of OPC and AAB with a model system, a calcite paste, that has been fully characterized in terms of macroscopic and microscopic behavior [3,4]. We interpret the rheological behavior of these suspensions in the framework of the classical fractal elasticity model proposed by Shih et al. [1], with an effort to relate the observed behaviour to the interparticle forces. Our goal is to develop a tool to interpret the role of the surface-solution equilibria in particle attraction and surface polymer adsorption potential.

2 Materials and methods

2.1 Samples preparation

1 An Ordinary Portland Cement CEM I 52.5 R powder (from Cementi Rossi, Italy, of picnometric density $3140 \text{ kg}\cdot\text{m}^{-3}$) was mixed directly in distilled water with w/c ratio varying from 0.5 to 0.3 (corresponding to $\phi = 0.39\text{-}0.51$). The mixing was done with a vortex stirrer (Ultra Turrax TD300 from IKA) for three minutes at increasing rotation speed from 2800 rpm to 5800 rpm.

2 The alkali activated slurry (AAS) was obtained by dispersing GGBS, (from Ecocem France, with $D_{50} = 11 \mu\text{m}$ and density of $2944 \text{ kg}\cdot\text{m}^{-3}$) in distilled water adding sodium carbonate Na_2CO_3 (reagent grade from Sigma Aldrich, density $2540 \text{ kg}\cdot\text{m}^{-3}$) as solid activator and calcium hydroxide $\text{Ca}(\text{OH})_2$ (ventilated hydrated lime CL90-S from Unicalce, Italy, density $2211 \text{ kg}\cdot\text{m}^{-3}$) as a setting and hardening accelerator. The binder formulation is: 91.5% of GGBS, 5% of Na_2CO_3 and 3.5% of $\text{Ca}(\text{OH})_2$ (density $2891 \text{ kg}\cdot\text{m}^{-3}$). The formulation involves stoichiometric amounts of Na_2CO_3 and $\text{Ca}(\text{OH})_2$, to optimize both the early setting and the long-term strength [12]. The binder to water ratio is varied from 0.5 to 0.3 (corresponding to $\phi = 0.41\text{-}0.53$). The mixing process is analogous to the one of CEM I.

3 As detailed in [3], to obtain calcite dense colloidal suspensions, Socal 31 calcite powder (Imerys, average particle diameter 75 nm, density 2710 kg m^{-3}) is also dispersed in distilled water. The maximum range of volume concentrations reached is $\phi = 5\text{-}30\%$. The mixing process was carried out in the same vortex stirrer for five minutes at an increasing mixing rate with the volume concentration from 2800 to 5800 rpm.

2.4 Rheological measurements

Rheological measurements were performed with a stress controlled rotational rheometer (Anton Paar, MCR 302).

Oscillation tests were made with a plate-plate geometry (Anton Paar, PP50 and PP25) at room temperature ($20 \pm 0.5^\circ\text{C}$). Plates were either roughened (AAS and

CEM I) or covered by sand paper (calcite), in order to avoid wall-slip together with an optimized gap for each system [3]. In particular, the gap is set to 2 mm for the CEM I and the AAS and 4 mm for the calcite paste. A moisture chamber was also used to avoid evaporation, particularly significant in the case of AAS. The “oscillation protocol” is constituted by: (i) a one-minute pre-shear at imposed shear rate of 10 s^{-1} (or deformation $\gamma = 10 \%$) in which the sample shear stress history is reset, (ii) a time structuration step at low deformation, in the range of elasticity of each system ($\gamma = 0.0005\%$ and $t = 2 \text{ min}$ for CEM I and AAS - $\gamma = 0.01 \%$ and $t = 5 \text{ min}$ for calcite) and frequency 1Hz in which the sample reaches a pseudo-steady state, increasing the elastic storage modulus G' and reaching a plateau after 1-2 minutes and (iii) an amplitude sweep at the imposed frequency of 1Hz with increasing deformation from 0.0001 to 10%. The measurements were performed at different volume concentrations, to explore the variation of the elastic properties. As detailed in [3], we extracted a linear storage modulus, G'_{lin} (i.e. storage modulus in the linear regime at low deformation), and a critical strain, γ_{cr} (i.e. value of deformation at the end of the G' linearity), and we compare the different behavior of the three systems as discussed below.

3 Results

Figure 1 and 2 show the influence of the volume fraction ϕ on the elasticity parameters G'_{lin} and γ_{cr} for the three systems.

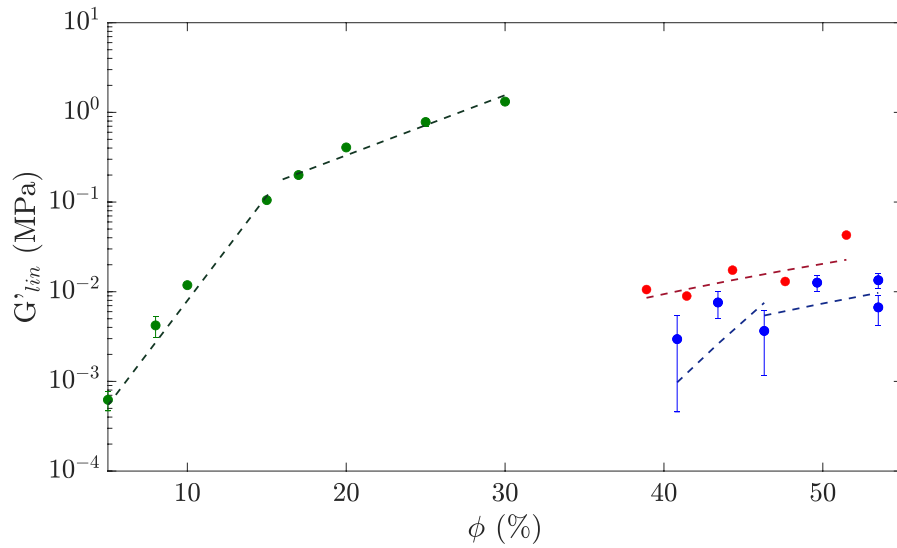


Figure 1: Linear storage modulus G'_{lin} as a function of the volume concentration ϕ for the three suspensions: calcite (green points), CEM I (red points) and AAS (blue points). The dashed lines represent the plot of the scaling model proposed by Shih et al. [1] as described in the discussion section. Error bars indicate the reproducibility of the results. Notice that the y-axis is in a logarithmic scale.

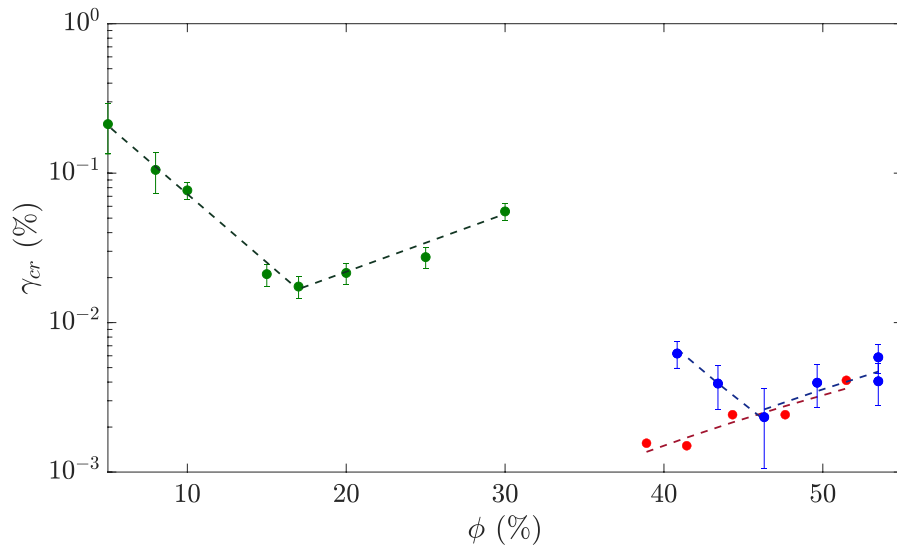


Figure 2: Critical strain γ_{cr} as a function of the volume concentration ϕ for the three suspensions: calcite (green points), CEM I (red points) and AAS (blue points). The dashed lines

represent the plot of the scaling model proposed by Shih et al. [1] as described in the discussion section. Error bars indicate the reproducibility of the results. Notice that the y-axis is in a logarithmic scale.

Starting with calcite, G'_{lin} constantly rises when ϕ increases, with a slope change around $\phi = 17\%$. This non monotonic trend is strongly confirmed by the ν_{cr} that shows a two-slope scaling behavior [3].

Both CEM I and AAS systems are shifted at a higher volume concentration range corresponding to a water to binder ratio between 0.5 and 0.3. This shift is mainly due to the different particle size and the nature of the interparticle interaction, as detailed in the discussion section.

Looking at both systems in Figure 1, they seem to have a similar behavior. In Figure 2 instead, CEM I shows a ν_{cr} which increases monotonically, while the AAS presents the same two-slope behavior observed for calcite.

4 Discussion

The amplitude sweeps have been measured, for each system, in the volume concentration range where the system has a gel-like behaviour. The system can flow under shear, with isolated flocs (clusters of particles) dispersed in the continuous interstitial solution, while at rest can form a continuous path of solid particles across the entire volume, which causes the appearance of elastic behaviour with $G' > G''$. We describe the elastic response to the small amplitude deformations according to a classical fractal model proposed by Shih et al. [1]. This model was originally proposed for colloidal suspensions such as our calcite paste, but it can be extended to all systems whose behaviour is controlled by colloidal surface forces, even if the particle dimensions are outside the Brownian motion regime [2].

The structure of the gel network is considered as constituted by fractal flocs (i.e. “repetitive highly porous aggregate composed of smaller primary particles” [13]). The rigidity and the deformation mechanism depend on the density and structure of the flocs, both function of the interaction forces between the particles [14]. Moreover, Shih et al. [1] define two regimes which depend on the compactness

of the particle network (i.e. fractal dimension d_f) and which give rise to different trends of G'_{lin} and γ_{cr} as a function of ϕ (Figure 1 and 2). At low ϕ , the floc is porous and deformable under shear. The bond between different flocs is strong compared to the intra-floc bonds, so that the weakest elements are the links between the particles inside the flocs. At high ϕ instead, the flocs are dense and rigid, and the deformation under strain occurs between different flocs. The power law scaling of the elastic modulus and critical strain are: (1) $G'_{lin} \propto \phi^A$, (2) $\gamma_{cr} \propto \phi^B$. Analogously the same equations can be extracted for a critical stress τ_{cr} , resulting from the product of G'_{lin} and γ_{cr} : (3) $\tau_{cr} \propto \phi^C$, where C is the sum of A and B. The scaling exponents are presented in Table 1 directly for the two regimes, respectively deformable and rigid flocs (DF and RF). The detailed derivation of these exponent is explained extensively in [1, 2].

	DF	RF
A ($G'_{lin} \propto \phi^A$)	$4/(3-d_f)$	$1/(3-d_f)$
B ($\gamma_{cr} \propto \phi^B$)	$-2/(3-d_f)$	$1/(3-d_f)$
C ($\tau_{cr} \propto \phi^C$)	$2/(3-d_f)$	$2/(3-d_f)$

Table 1: Exponent of the power law for G'_{lin} and γ_{cr} as a function of the fractal dimension d_f for the different regimes (i.e. DF, Deformable Floc and RF, Rigid Floc).

As shown in Table 1, the slope of the exponent is always positive, except for γ_{cr} in the deformable regime. This can be observed in Figure 2 for the calcite and AAS at lower ϕ in the respective volume concentration range. From the scaling laws of G'_{lin} , γ_{cr} , τ_{cr} as a function of ϕ , the fractal dimensions d_f are calculated and reported in Table 2 for the three systems at rest (i.e. small amplitude oscillation measurements). We expected that, under shear (i.e. flow measurements), the continuous, percolated structure formed at rest is destroyed, forming isolated rigid flocs with a resulting floc fractal dimension closer to 3.

	d_f (DF)	d_f (RF)
CEM I	-	2.71
AAS	2.73	2.75
CaCO₃	2.23	2.61

Table 2: Fractal dimension d_f calculated for the three different systems in the two different regimes (i.e. DF, Deformable Floc and RF, Rigid Floc).

We can notice that for both calcite and AAS suspensions, both regimes are present. As extensively discussed in [2], the presence of both regimes, when exploring the influence of volume fraction only (i.e. no external forces), is not common in colloidal systems and it is surprising to find it also in a non-colloidal one (i.e. AAS). This behavior for our AAS is the sign of weak inter-particle interactions and flocs which become stiffer when growing larger.

Differently, CEM I, despite the similarity with AAS in the high concentrated paste condition state, is presenting only the rigid floc regime throughout the range of ϕ . Before going into detail about the nature of the three different systems, the different deformation mechanisms are schematically illustrated according to the Shih et al. [1] scaling fractal model in Figure 3.

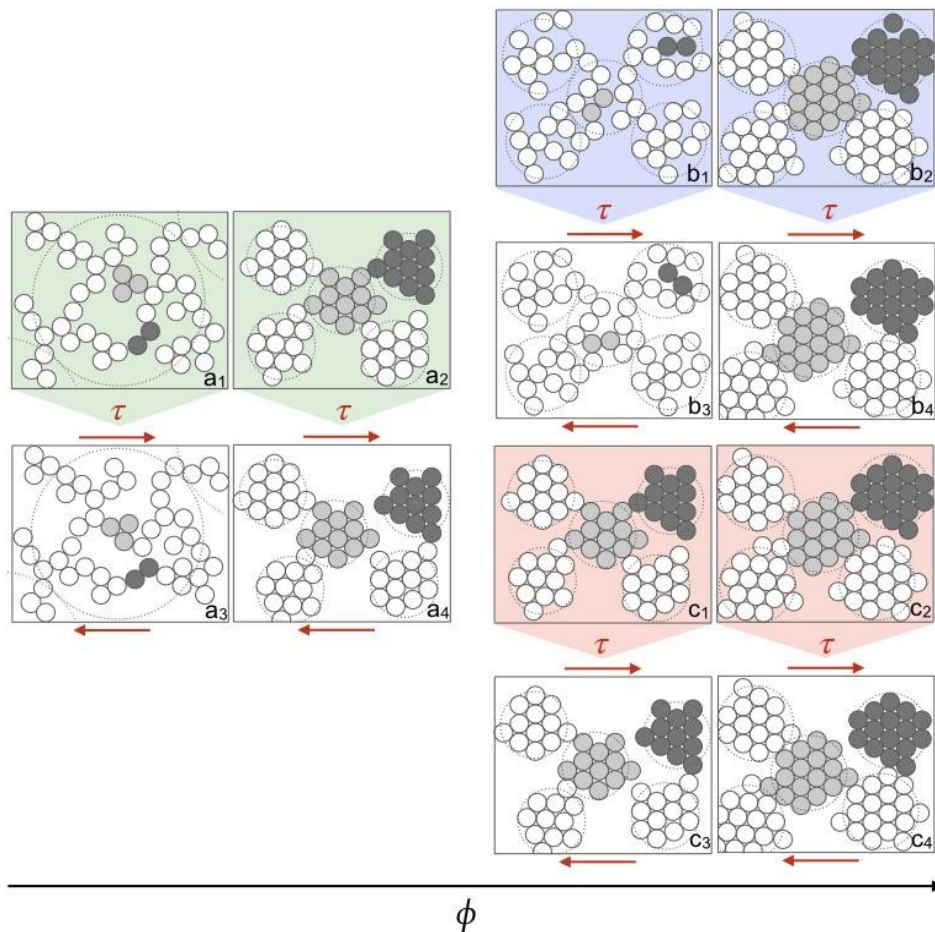


Figure 3: Schematic floc deformation mechanism at different volume concentration ϕ for the three systems: calcite (a₁-a₄), AAS (b₁-b₄) and CEM I (c₁-c₄). The dashed lines represent the floc. The upper part of each system (light colored) represents flocs at rest and the lower part the new floc configuration after imposing a deformation. Few particles or flocs are colored (i.e. light or dark grey) to help visualize the floc reconfiguration through the movement of the individual particles.

In particular, if we compare Figure 2 with Figure 3, we can recognize the regime of floc deformation (a₁ to a₃, b₁ to b₃) and the regime of rigid flocs (a₂ to a₄, b₂ to b₄, c₁ to c₃, c₂ to c₄).

The different deformation regimes determine microstructural differences of the three systems. The calcite used in this study is a nano-powder which creates, once suspended with water, weak electrostatic attraction between particles. The nature of these interaction (DLVO) was fully described (as detailed in [3]) thanks to the study of the rheology and the physico-chemistry of the suspensions.

Systems like CEM I and AAS are constituted by micrometric particles and, when suspended in water, interact via short-ranged electrostatic and correlation forces that produce short distance electrostatic forces [11]. This explains the narrower volume fraction range at which an CEM I and AAS elastic pastes are formed and which are really sensitive to the complex chemistry of the solution.

5 Conclusion & Perspective

The observed differences between the rheology of cement and AAS illustrate the different cohesivities of the two pastes. We show on this study that rheology is an important tool to investigate the paste cohesivity, deformation and flow mechanisms, and surface properties. In a follow-up study, we plan to investigate the rheology of the two systems in the presence of superplasticizers, and aim at elucidating the reason behind the high effectiveness of common superplasticizers on cement but not on alkali activated materials.

6 Acknowledgements

We thank Österreichische Bautechnik Vereinigung (ÖBV) and Österreichische Forschungsförderungsgesellschaft (FFG) for their support.

Bibliography

- [1] Shih, W.-H., Shih, W. Y., Kim, S.-I., Liu, J. and Aksay, I. A.: Scaling behavior of the elastic properties of colloidal gels. *Physical Review A*, 1990.
- [2] Bellotto, M.: *Cement paste prior to setting: A rheological approach*. Cement and Concrete Research, 2013
- [3] Liberto, T., Le Merrer, M., Barentin, C., Bellotto, M., and Colombani, J.: Elasticity and yielding of a calcite paste: scaling laws in a dense colloidal suspension. *Soft Matter*, 2017.
- [4] Liberto, T., Barentin, C., Bellotto, M., Colombani, J., Costa, A., Gardini, D. and Le Merrer, M: Simple ions control the elasticity of calcite gels via interparticle forces. *Journal of Colloid and Interface Science* 2019.
- [5] Shi, C., Roy, D. and Krivenko, P., *Alkali-activated Cements and Concretes*. Taylor & Francis, 2006.
- [6] Luukkonen, T., Abdollahnejad, Z., Yliniemi, J., Kinnunen, P. and Illikainen, M.: One-part alkali-activated materials: A review. *Cement and Concrete Research*, 2017.
- [7] Habert, G., d'Espinose de Lacaillerie, J.B. and Roussel, N.: An environmental evaluation of geopolymer based concrete production: reviewing current research trends. *Journal of Cleaner Production*, 2011
- [8] Purdon, A. O.: Improvements in processes of manufacturing cement, mortars and concretes. British Patent GB427227A, 1935.

- [9] Buchwald, A., Vanooteghem, M., Gruyaert, E., Hilbig, H., and De Belie N: Purdocement: application of alkali-activated slag cement in Belgium in the 1950s. *Materials and Structures*, 2015.
- [10] Palacios M., Houst Y.F., Bowen P. and Puertas F.: Adsorption of superplasticizer admixtures on alkali-activated slag pastes. *Cement and Concrete Results*, 2009.
- [11] Jönsson, B., Nonat, A., Labbez, C., Cabane, B. and Wennerström, H.: Controlling the Cohesion of Cement Paste. *Langmuir*, 2005.
- [12] Bellotto M., Dalconi M.C., Contessi S., Garbin E. and Artioli G.: Formulation, performance, hydration and rheological behavior of ‘just add water’ slag-based binders. *Proceedings of the 1st International Conference on Innovation in Low-Carbon Cement and Concrete Technology*, London 2019.
- [13] Jarvis, P., Jefferson, B. and Parsons, S. A.: Measuring Floc Structural Characteristics. *Reviews in Environmental Science and Bio/Technology*, 2005.
-
- [14] Shih, W.Y., Shih, W.H. and Aksay, I.A.: Elastic and yield behavior of strongly flocculated colloids. *Journal of the American Ceramic Society*, 1999.