CONTROLLING THE ELASTICITY OF CALCITE SUSPENSIONS WITH SIMPLE IONS

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INTRODUCTION

Calcite is an ubiquitous mineral employed in many industrial fields such as paper filling, pharmaceutical, art or construction. In particular the suspension of its particles is used to mimic early stage cementitious materials. In order to control the mechanical properties of calcite paste it is necessary to understand the role of the interaction forces between its particles. In this regard, this study show how a macroscopic quantity of the calcite suspensions, namely the elasticity, measured by rheological measurements can be linked to microscopic interactions, via DLVO analysis. Our calcite pastes are weakly attractive systems, showing a typical colloidal gel behavior, and characterized by an elastic shear modulus and a critical strain. We have tuned the interaction forces between particles by addition of simple ionic species (Ca^{2+} and OH^-). Rheological measurements are compared to DLVO calculations, obtained by chemical speciations and ζ potential measurements on dense suspensions.

MATERIALS AND METHODS

Socal 31 calcite powder (Imerys) with an average particle diameter of 70 nm is dispersed in various solutions to obtain several calcite suspensions [1,2]. The initial calcite volume concentration is fixed to $\phi = 10\%$. To investigate the effects of simple ionic additives, we disperse calcium hydroxide $Ca(OH)_2$ (concentrations c ranging from 3 to 50 mM) or sodium hydroxide NaOH (concentration 100 mM) in deionized water.

Rheological measurements are made with a plate-plate geometry (gap width 1 mm)[1,2]. The measurements consist in a pre-shear step with 1 minute imposed shear rate of $\dot{\gamma} = 10$ s^{-1} and then a constant deformation of $\gamma = 0.01\%$ at frequency $f = 1$ Hz during 10h. In particular, the imposed deformation is small enough to remain in the linear regime [1] and allows to measure the temporal evolution of the storage modulus $G'(t)$ of the samples. **DLVO calculation** (Derjaguin-Landau-Verwey-Overbeek) between parallel planes [2] is used to characterize the strength of particle interaction [3]. **Zeta potential measurements** are carried out directly on the concentrated calcite suspensions with an electroacoustic technique (ZetaProbe)[2,4]. The suspension **chemical speciations** (i.e. full ionic compositions) are obtained with the freeware Visual MINTEQ [2,5]. For all the samples, pH measurements are made directly on the fresh suspensions.

RESULTS AND DISCUSSION

As shown in Figure 1, addition of calcium hydroxide improves the initial workability of the paste by lowering the elastic modulus of the paste (G'), which is further recovered upon carbonation (in time) in contact with atmospheric carbon dioxide. To estimate the change of interaction nature with the calcium hydroxide concentration, we have computed the value of the DLVO potential and its

maximum energy barrier $W_{\max}$ against pH, as shown in Figure 2(b). Its evolution is strongly non linear, with a sharp maximum at pH $\simeq$ 12. The initial elastic modulus of the paste in the same pH range is presented in Figure 2(a). The evolution of interaction potential and mechanical property are strongly correlate. The weaker the attraction, the softer the gel. The $G'(0)$ minimum and $W_{\max}$ maximum match perfectly at pH $\approx$ 12. Below this pH, the main effect is a change in surface potential with calcium concentrations, while at high pH, modifications of the ionic strength and Debye lengths are dominant. We also demonstrate that the addition of NaOH completely screens the charges and leads to a strongly interacting and rigid paste [2].

CONCLUSION

We have shown in this study how simple ions modifies significantly the mechanical behavior of a calcite paste. We found a direct correlation between the elastic modulus of colloidal calcite paste and the energy barrier calculated using the classical DLVO potential. A practical consequence of our findings is that calcium hydroxide could be used as an admixture to get more workable calcium carbonate pastes, considering that the induced extra-fluidity spontaneously disappears, by simple contact with air, to give good final mechanical properties. The perspective of this work is to applied an analogous procedure to cementitious material in order to connect the macroscopic behavior of the paste with the microscopical interaction.

REFERENCES

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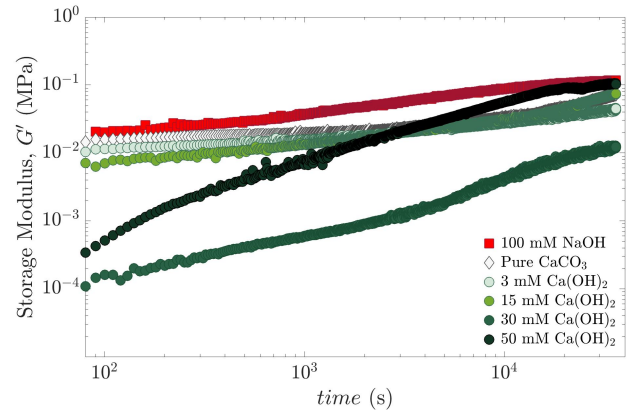
Figure 1: Time evolution of the storage modulus G' of calcite suspensions of concentration $\phi = 10\,\%$, for increasing c and a sample containing NaOH.
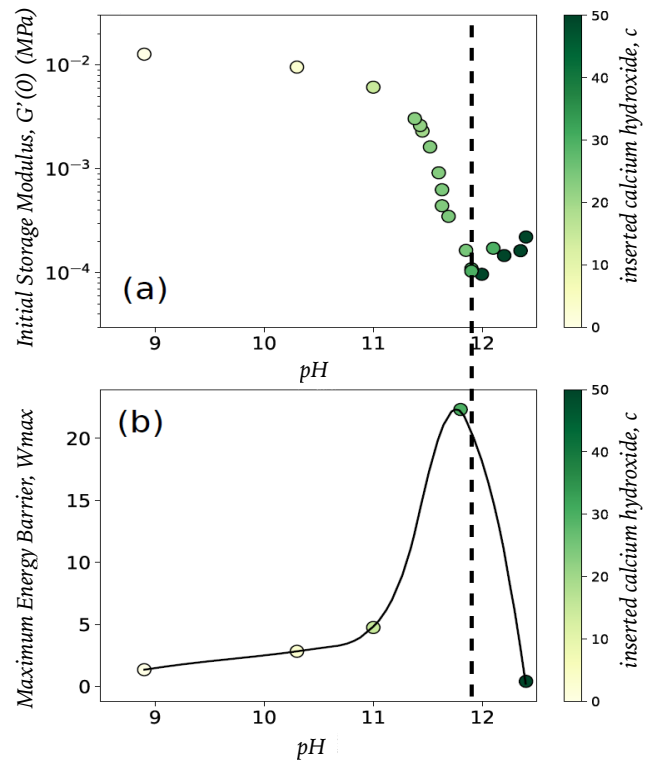
Figure 2: (a) Initial storage modulus $G'(0)$ as a function of pH. (b) Maximum energy barrier, $W_{\max}$ as a function of pH. The different data points correspond to various Ca(OH)$_2$ oncentrations (c).