PHYSICAL REVIEW E **84**, 066121 (2011)

Pressure solution as origin of the humid creep of a mineral material

Edgar Alejandro Pachon-Rodriguez,[1] Emmanuel Guillon,[2] Geert Houvenaghel,[2] and Jean Colombani[1,*]
[1]*Laboratoire de Physique de la Matière Condensée et Nanostructures, Université de Lyon, Université Claude Bernard Lyon 1, CNRS, UMR 5586, Domaine Scientifique de la Doua, F-69622 Villeurbanne Cedex, France*
[2]*Lafarge Centre de Recherche, 95 Rue du Montmurier, BP 15, F-38291 Saint Quentin Fallavier Cedex, France*

(Received 10 November 2011; published 27 December 2011)

The significant enhancement of the creep of plasterboard by a humid environment is well known in the building industry. But despite its strong impact on the material durability, its origin remains unexplained. We present here experimental evidence that the creep of wet set plaster is driven by the dissolution kinetics of gypsum, its major component, in intercrystalline water layers. Linking this surface molecular behavior to a macroscopic mechanical property has been made possible by the establishment, using holographic interferometry, of an accurate method of convection-free dissolution measurement, and by the possibility of tuning the dissolution kinetics of the material by the use of additives. Although it is well known in geological contexts, this dissolution-creep correlation had not yet been observed outside this field. It enables one to propose pressure solution as the mechanism of the wet creep of set plaster and sheds light on the humid creep of polycrystalline mineral materials.

DOI: 10.1103/PhysRevE.84.066121 PACS number(s): 62.20.F−, 62.20.Hg, 42.40.Kw, 82.20.Pm

I. INTRODUCTION

Plasterboard is a universally employed building material. It is a cheap, light, insulating, and fireproof solid, which compensates for its weak mechanical strength. This material has been used for decades, yet the understanding of its mechanical behavior is still poor. One striking example is the enhancement of the creep of set plaster by a humid environment [1]: Although this everyday life phenomenon has been known for a long time, its origin remains unknown. It constitutes a strong limitation of the durability of this material, especially in regions with a humid climate.

Here, we demonstrate that the creep strain rate of wet set plaster is driven by the dissolution kinetics in water of the mineral constituting the material. This feature enables us to propose a model for the creep mechanism, and to give elements to improve the set plaster mechanical behavior. It also gives clues to understand the humid creep of more complex polycrystalline mineral materials.

Set plaster is constituted of entangled micrometer-size elongated gypsum crystals ($CaSO_4 \cdot 2H_2O$), obtained from the hydration of calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$). Most of the adjacent crystallites are considered to be linked via a thin water film. Immersed in water, the thickness of this liquid slab ($\sim$10 nm) is thought to be fixed by the competition between the van der Waals attraction between the crystallites through the water film and the repulsion of the Debye layers formed close to the surfaces, as in flocculated colloids [2]. In a humid atmosphere, capillary forces at the ends of the liquid film should contribute also to the intercrystalline attraction and strengthen the material [2]. According to this view, the mechanical strength of set plaster is a consequence of the attraction between gypsum faces through the confined water, the capillary forces exerting on the boundaries of the water layers, and the number of bonds between microcrystals, as well as their entanglement [3]. A firmly assessed feature is that plastic strain originates in intercrystalline phenomena, not in the deformation of individual microcrystals [4]. The swelling of the water layer (due to the increase in relative humidity or the material soaking in water) is thought to weaken the intercrystalline interaction and to facilitate the sliding between the gypsum needles. This assumption has enabled the interpretation of various mechanical properties of set plaster in the presence of water: the fall of rigidity [5,6] and compressive strength [7] with the increase of humidity, the fall of bending strength when the material is wetted [8,9], and the reversibility of the hardness decrease induced by the material wetting [9]. Nevertheless, this mechanism has not yet been proven to be the origin of creep in a humid or wet environment [2]. Because the needle-sliding model does not allow one to interpret humid creep, a different origin has been sought and it has been proposed that the creep derives from the solubility of gypsum in water. But several studies have assessed clearly that no direct correlation exists between the mechanical properties of gypsum-based materials soaked in a liquid and the solubility of gypsum in this liquid. One study has measured the compression creep of set plaster impregnated by a variety of dissolving and nondissolving solvents [10]. Another one has used the same methodology to investigate the flexure strength of set plaster [9]. A third one has studied the compaction creep of gypsum aggregates in water and saline water [11]. All have concluded that there is an absence of a clear link between strength and solubility. Our work investigates not the solubility, i.e., the gypsum-water chemical equilibrium, but the dissolution kinetics, i.e., the way to this equilibrium. Indeed, we conjecture that the humid creep is a consequence of the dissolution of the mineral in the intercrystalline water, with this dissolution stemming from the local stress in the solid due to the external load. This water-mediated creep mechanism is widespread in geological situations and contributes largely to the upper crust deformation and rock formation [12], but it has never been reported in materials physics to date.

Experimental validation of this hypothesis was not possible until now because of limitations in the knowledge of gypsum dissolution kinetics. Although the solubility of gypsum is well known, no consistency exists in the literature among the measurements performed by various devices on its dissolution

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*jean.colombani@univ-lyon1.fr

kinetics. A variation of several orders of magnitude of the dissolution rate constant can be found [13]. This lack of accuracy impeded a quantitative check of the hypothesis. The dispersion of the results is a consequence of the fact that in all experiments, the solvent was stirred, adding convection to dissolution. An analysis of the hydrodynamical conditions of the various techniques used in the experiments reported in the literature has permitted one to compute the convective contribution in the measured dissolution rate in each case. An extrapolation of all of these results to a convection-free situation has allowed us to determine the pure dissolution rate constant of gypsum in water, $k = 7 \times 10^{-5}$ mol m^{-2} s^{-1} [13]. To circumvent experiments with forced convection, we established a protocol, which makes use of holographic interferometry and enables a direct access to the surface reaction rate constant of gypsum [14]. In this setup, the solvent is stagnant and hence the pure dissolution rate constant is accessible without hydrodynamical assumptions. Its value was measured, $k = (5 \pm 2) \times 10^{-5}$ mol m^{-2} s^{-1}, and agreed perfectly with the value deduced from the analysis of the literature, assessing thereby the validity of the experimental methodology. The accuracy of the method is now sufficient to allow the investigation of the dissolution rate constant of gypsum in water in the presence of various additives. Indeed, whereas the origin of humid creep remains unknown, anticreep adjuvants, which reduce the strain due to humid creep, have been discovered and are used industrially. Their undeniable efficiency is, again, unexplained. We have taken advantage of this empirical knowledge. To estimate the link between wet creep and dissolution, we have carried out two types of experiments: (1) we have measured the dissolution rate of gypsum in water containing an additive and (2) we have tested the wet creep of set plaster containing the same additive.

II. MATERIALS AND METHOD

The investigated additives are a tartaric acid-boric acid mixture (additive no. 1), a sodium salt of a polyamino carboxylic acid (additive no. 2), two commercial versions of a phosphonate potassium salt (additives no. 3 and no. 4) and a sodium phosphate salt (additive no. 5). These adjuvants are all known to form complexes with the calcium ion. The interest of these salts lies in their simultaneous influence on set plaster creep and gypsum dissolution, not in the chemical details of their chelating action at the surface of gypsum crystals. The formed compounds may experience selective adsorption on the various crystallographic planes of gypsum. They may thereby modify the crystal habit in the final product. Some salts are, for instance, known to turn the habit from acicular to columnar or lenticular [15]. We have, therefore, carried out scanning electron microscope observations of the set plaster casted with the various additives. For all of the samples, the microcrystals show the characteristic needlelike shape with roughly the same dimensions. Two examples are shown in Fig. 1.

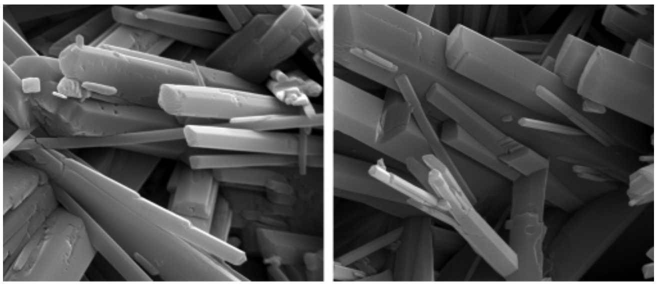

FIG. 1. Scanning electron microscope images of the microstructure of set plaster elaborated with additive no. 2 (left) and no. 5 (right). The dimension of the images is 12.7×11.0 μm^2.

During the dissolution experiments, a freshly cleaved gypsum single crystal is deposited at the bottom of a transparent cell containing the solvent (water + additive) at rest. The solid dissolves and the concentration changes accordingly in the fluid. The concentration evolution induces a change of the index of refraction. This change is monitored in real time by a digital holographic interferometry setup. From the fringe pattern, the concentration evolution $c(z,t)$ as a function of the vertical position z and time t can be computed. An analytical expression of $c(z,t)$ is obtained from solving Fick's equation with the relevant boundary conditions [14]. Fitting the experimental data with the theoretical analytical expression allows one to determine the diffusion coefficient D of the gypsum dissolved species in the solution of additive and the dissolution rate constant k of gypsum in this solution. This rate constant is the fundamental thermodynamic coefficient characterizing the kinetics of the reaction.

For the three-point bend creep tests, the parallelepiped samples in set plaster are elaborated with finely ground plaster (β-hemihydrate of calcium sulfate) poured in water containing the additive, with a water-plaster weight ratio of 0.8, leading to a 57% porosity. The hemihydrate was obtained from the dehydration of natural gypsum of the same origin as the one used in the holographic interferometry experiments. The mixture is stirred, until it forms a homogeneous paste, and casted. During this process, hemihydrate hydrates to gypsum, the typical microstructure of set plaster forms, and the paste solidifies. The samples are subsequently maintained for 24 h in a closed vessel to achieve complete hydration and are stored, until the test, in a saturated solution of calcium sulfate to avoid dehydration of the mineral [8]. The parallelepiped samples have length $l = 180$, width $w = 20$, and height $h = 20$ mm. For the bending creep experiments, the set plaster beams are soaked in a saturated aqueous solution of calcium sulfate, so that the mineral is in the same environment as in the holographic interferometry experiments. The solution is saturated with calcium sulfate in order to probe stress-induced dissolution, not simple dissolution. The experimental device is the standard three-point bending setup used for the investigation of the flexure properties of ceramic materials [16]. The samples are loaded in the middle on the top surface and supported at their ends, and their deflection δ is recorded. For each additive, experiments at different applied loads P and various concentrations (between 0.05 and 0.5%) are carried out. The maximum compressive stress σ and the compressive strain ε at the center of the beam are determined as $\sigma = 3PL/(2wh^2)$ and $\varepsilon = 6h\delta/L^2$, with L as the support span. Set plaster is known to experience important subcritical crack growth due to its heterogeneous microstructure. Therefore, the maximum stress value for each additive is chosen as 20% of the measured flexural strength, under which this effect is expected to remain minimal [1,17].

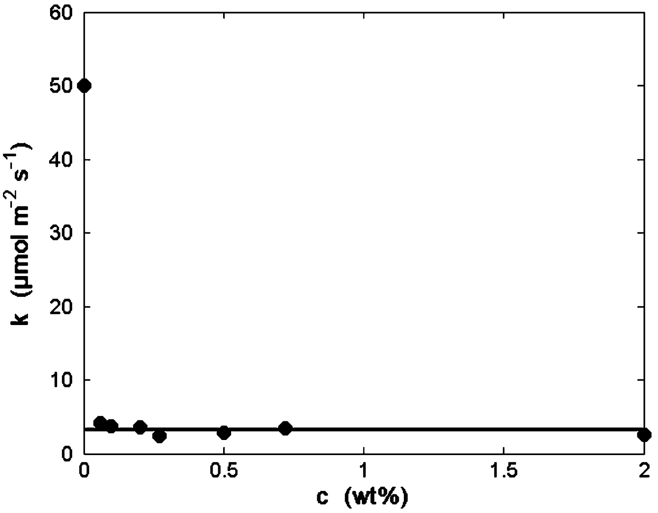

FIG. 2. Dissolution rate constant of gypsum in an aqueous solution of additive no. 5 measured by holographic interferometry as a function of the additive mass fraction. The horizontal line is the average value.

So the investigated stresses range between 0.244 and 0.626 MPa.

III. RESULTS

The holographic interferometry experiments provide three main results. First, the dissolution rate constant of gypsum in the additive solutions is shown to be independent of the concentration of additive, down to a concentration as low as 0.05 wt%. An example of this independence is displayed in Fig. 2. It is a consequence of the fact that dissolution is a surface process. As soon as the quantity of molecules in the solution is high enough to cover all of the active sites of the crystal surface, the effect of the additive on the reaction rate is maximum. Second, the rate constants for the various additives have values ranging from 74 (additive no. 1) to 3 (additive no. 5) μmol m^{-2} s^{-1}. We stress again that these values characterize exclusively the purely molecular surface behavior of dissolving gypsum, without any influence of the diffusion or convection above this surface. Third, with the additive concentration remaining small, the diffusion coefficient of dissolved gypsum in the additive aqueous solutions does not vary significantly. Its value ranges from 4×10^{-10} to 7×10^{-10} m^2 s^{-1} for the various adjuvants.

In addition, we have performed independent induced coupled plasma atomic emission spectroscopy measurements and we found that the gypsum solubility s in the adjuvant solutions never departs from its value in pure water (15 mmol kg^{-1}, i.e., 2 g L^{-1}), due to the small concentration of adjuvant.

The bending creep test results are plotted as $\varepsilon(t)$ curves. Figure 3 shows the measurements for the $\sigma = 0.244$ MPa case. As evidenced in the inset in Fig. 3, all of the curves obey a power law $\varepsilon = A\,t^n$, represented by straight lines in a log-log plot. The exponent n decreases with the increasing anticreep efficiency, from 0.69 (additive no. 1) to 0.34 (additive no. 5). The strain rates $d\varepsilon/dt$ are obtained by differentiating the experimental $\varepsilon(t)$ curves with respect to time. For each additive, the strain rates do not depend on the concentration, except for the smallest ones ($\lesssim$0.1 wt%) where the anticreep effect decreases.

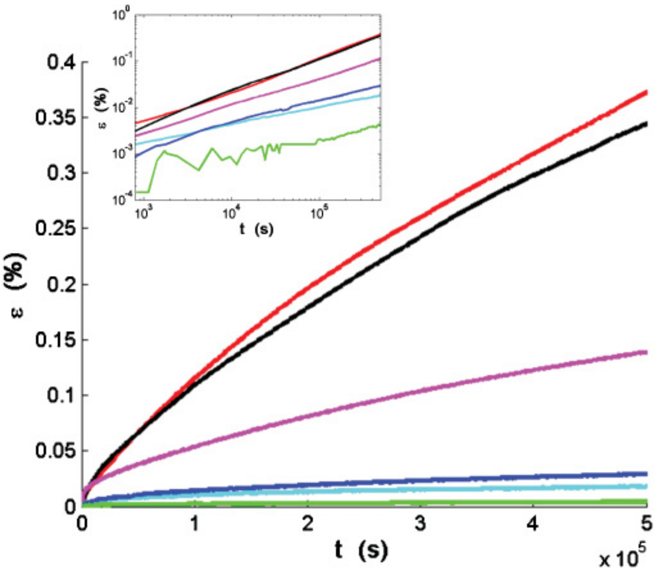

FIG. 3. (Color online) Evolution in time of the compressive strain at the center of a set plaster beam during a bending creep test in water saturated with calcium sulfate for a 0.244 MPa stress. From upper to lower curve: additive no. 1 (red); pure water (black); additive no. 2 (pink); additive no. 3 (blue); additive no. 4 (light blue); additive no. 5 (green). Inset: log-log plot of the same curves.

IV. DISCUSSION

To analyze these results in detail, we have to establish a microscopic physical model for the wet creep. The external flexure load induces local compressive stresses between adjacent gypsum needles, via the intercrystalline water layer. This stress provokes a change of the chemical potential of the solid. The solubility of gypsum in the confined water then enhances, in order for the chemical potential of the liquid to equalize with the stressed solid one, to recover chemical equilibrium. The resultant dissolved species diffuse through the water film, and precipitate at unstressed surfaces of the solid. This dissolution-diffusion-recrystallization sequence leads to a plastic strain, accommodating the stress (Fig. 4). This process, common in geological contexts, has aroused a wealth of experimental and modeling studies. But despite this effort, a considerable discrepancy between experimental and numerical results still exists [18]. Whereas no unified view of the creep kinetics has been proposed, the strain evolution with time can often be fitted by a power law with an exponent, $n < 1$. This exponent varies with (i) the structure of the intergrain contact, (ii) the nature of the slowest step of the mechanism (reaction at the interface or transport in the intergranular space), driving the process, and (iii) the grain geometry, packing, size distribution, etc. [19]. For instance, the huge influence of the width of the grain size distribution on the strain rate has been recently highlighted [18]. This phenomenon has been studied in the particular case of gypsum aggregates under hydrostatic and uniaxial loads, but again without the emergence of a coherent behavior of the creep kinetics [11,20]. In the absence of

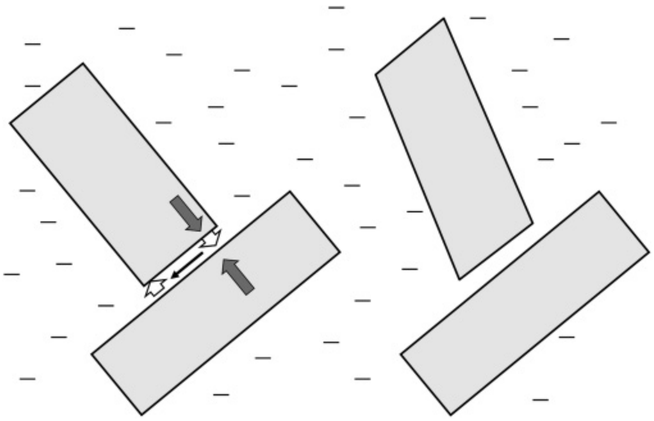

FIG. 4. Schematics of pressure solution creep in wet set plaster. Two gypsum needles (see Fig. 1) are immersed in a saturated solution. The applied stress on the material induces a local compressive stress (gray arrows), which leads to the dissolution (white arrow), diffusion in the nanometric interneedle aqueous solution layer (black arrow), and precipitation (inverted white arrow). This matter transfer results in a plastic strain.

an established comprehensive law, enabling one to estimate quantitatively the role of the pressure solution on the strain rate, first order models are used. For instance, in Raj's model, the instantaneous strain rate of an unique cubic grain is derived [21]: If diffusion is the limiting stage, then the strain rate scales as $d\varepsilon/dt \sim \sigma D s/d^3$, where d is the mean size of the solid contacts where dissolution proceeds; if dissolution is the limiting stage, then it scales as $d\varepsilon/dt \sim \sigma k s/d$. This model is oversimplified for the structure of our material, but it can help us to identify the relevant correlations.

Therefore, we have checked the dependence of $d\varepsilon/dt$ on D and k, measured by holographic interferometry. The value of the diffusion coefficient of the dissolved species of gypsum in water containing the various additives is always quasisimilar to its value in pure water (like gypsum solubility s), whereas the $[d\varepsilon(t)/dt]/\sigma$ ratio of set plaster elaborated with these additives spans over more than two orders of magnitude. An example of this independence on D is given in Fig. 5. It can be immediately concluded that we do not face diffusion-driven pressure solution creep. So we have drawn the evolution with time of $[d\varepsilon(t)/dt]/(\sigma k)$, which remains constant in Raj's model if the process is reaction-controlled pressure solution creep (Fig. 6). After a transient regime, the parameter shows a slow evolution with time (linked to the complex microstructure of set plaster, compared to Raj's model), during which all of the additives stay relatively collapsed. The dispersion of the results is quite large but is seen to be equal to the experimental uncertainty, with the oscillations of the values of additives no. 3–5 being responsible for this dispersion. To emphasize the link between the strain rate and reaction kinetics, Fig. 7 shows $[d\varepsilon(t)/dt]/\sigma$ as a function of k, for three times. A strong correlation can be seen between both quantities, which does not change significantly with time. Due to the complex microstructure of the material, the functional dependence of $[d\varepsilon(t)/dt]/\sigma$ on k is not a simple proportionality as in Raj's model. Rather, it is a power law with an exponent varying from 1.4 to 1.7 between the boundary times in Fig. 7, i.e., the beginning of the steady state ($t \simeq 0.4 \times 10^5$ s) and the end of the experiment ($t = 5 \times 10^5$ s).

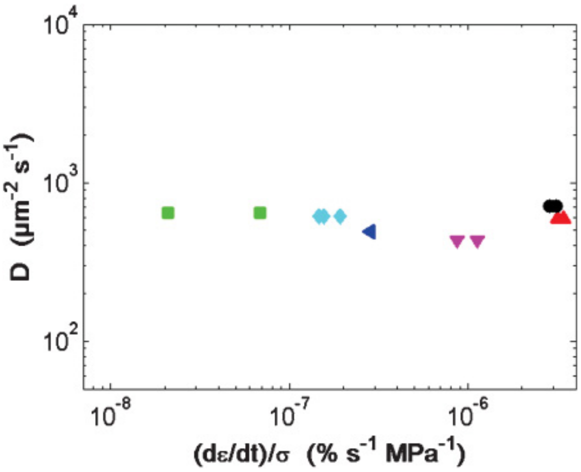

FIG. 5. (Color online) Diffusion coefficient of dissolved gypsum in a solution of a given additive, as a function of the ratio of the strain rate at $t = 1 \times 10^5$ s and of the applied stress, for the flexure wet creep of a set plaster beam elaborated with the same additive. Red upward-pointing triangles: additive no. 1; black circles: pure water; pink downward-pointing triangles: additive no. 2; blue left-pointing triangles: additive no. 3; light blue diamonds: additive no. 4; green squares: additive no. 5.

Much work has been carried out on the nature, shape, size, and evolution during creep of the contact between the solids; the access to d, even in simple geometries is a highly delicate task [22,23]. But no dependence of the strain rate on d has to be introduced here, which should be a consequence of the above-mentioned similarity of the microstructure of all of the samples: the additive used during their elaboration does not modify significantly the crystal habit and intercrystalline contact structure.

The results in Fig. 7 support the hypothesis of an interface-driven pressure solution creep. The faculty to (i) measure the

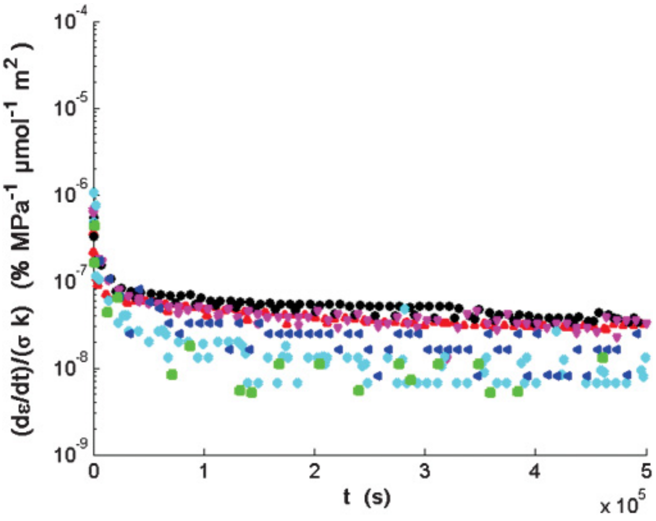

FIG. 6. (Color online) Strain rate normalized by the applied stress and dissolution rate constant as a function of time for all experiments. The color code is the same as in Fig. 5.

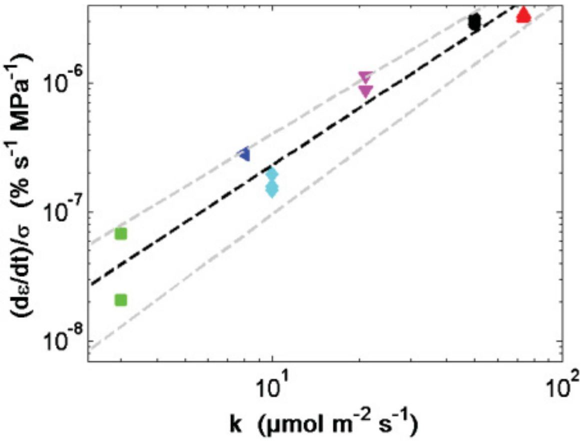

FIG. 7. (Color online) Ratio of the strain rate at $t = 1 \times 10^5$ s and of the applied stress, for the flexure wet creep of a set plaster beam elaborated with a given additive, as a function of the dissolution rate constant of gypsum in a solution of the same additive. The color code is the same as in Fig. 5. The black dashed line is a linear fit of the data. The upper gray dashed line corresponds to the same linear fit at times $t = 0.4 \times 10^5$ s (beginning of the stationary state of the creep curves) and the lower line corresponds to time $t = 5 \times 10^5$ s (end of the experiment).

pure dissolution rate constant of a material and (ii) tune this rate constant thanks to known adjuvants, has thus permitted to correlate the creep kinetics directly to the kinetics of the chemical reaction at the interface. Thereby, this methodology has permitted us to establish that the wet creep of set plaster is likely to originate in the dissolution-recrystallization of gypsum needles, rather than in the sliding between these needles [24].

Finally, it should also be noted that the creep exponent $0.34 \approx 1/3$ of the more efficient anticreep additives is reminiscent of other pressure solution creep situations, and has been interpreted as a consequence of the universal behavior of shrinking liquid films, experienced by the confined water layers with a mechanism similar to spinodal decomposition [12].

V. CONCLUSION

By comparing the influence of several salts on the chemical behavior of the gypsum-water interaction and the wet creep of set plaster, we have evidenced the correlation between the dissolution velocity and wet creep strain rate of the material. This result permits us to propose that pressure solution creep is the mechanism of deformation and to state that dissolution is the limiting stage of the creep kinetics. This statement opens the way to the methodic search for new anticreep methods or additives. This study shows that pressure solution creep is not limited to geological situations, as the involved space and time scales could suggest, and is also susceptible to play a role in the wet creep of materials structurally close to set plaster, like hydraulic cements [25], polycrystalline or composite ceramics [26], and porous minerals, and should help to interpret their long-term wet mechanical behavior. The present study characterizes the behavior of a material completely saturated with water. Further studies will be necessary to investigate its behavior in the presence of water vapor, where the presence of liquid water around the crystallites is limited to capillary menisci.

ACKNOWLEDGMENTS

We thank Elisabeth Charlaix, Ellis Gartner, François Renard, and Dag Dysthe for fruitful discussions. This work was supported by Lafarge Centre de Recherche, Région Rhône-Alpes and CNES.

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