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Edgar Alejandro Pachon-Rodriguez[a], Emmanuel Guillon[b], Geert Houvenaghel[b], Jean Colombani[a,*]

[a]*Institut Lumière Matière; Université de Lyon; Université Claude Bernard Lyon 1; CNRS, UMR 5306; Domaine scientifique de la Doua, F-69622 Villeurbanne cedex, France*

[b]*Lafarge Centre de Recherche; 95, rue du Montmurier, BP 15, F-38291 Saint Quentin Fallavier cedex, France*

Abstract

Gypsum plaster exhibits a dramatic creep when placed in a very humid environment. We have combined mechanical tests of wet bending creep of set plaster and holographic interferometry measurements of dissolution rate and diffusion coefficient to look for the origin of this wet creep. Both these experiments have been performed in absence and presence of various known anti-creep admixtures. It appears that the creep rate and dissolution rate are strongly correlated. This correlation has allowed to propose surface-driven pressure solution creep as mechanism of wet creep of gypsum plaster, i.e., the sequence dissolution in the grain boundary water/diffusion/precipitation at the grain surface. An order of magnitude analysis shows that this dissolution-diffusion-recrystallization series can also contribute to the creep of hydrated Portland cement.

*Corresponding author, jean.colombani@univ-lyon1.fr

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1. Introduction

Hydraulic cements are mineral powders that harden under water, and subsequently remain cohesive in presence of water. They constitute the main materials of the building industry, used under the form of pastes to enable molding in the desired shape. Portland cement and gypsum plaster are the most used hydraulic binders because of their availability, low cost and easy installation. Hardened Portland cement and its derivatives (mortar, concrete) has also the virtue to be load-bearing, and hydrated plaster of Paris to be light, isolating and fire resistant. One of their limitations is their long-time plastic strain, or creep, mainly indoor for gypsum plaster and outdoor for hardened Portland cement. For gypsum, this creep is strongly enhanced by the presence of humidity.

Being chemically and structurally much simpler than hydrated cement pastes, this study is devoted to the creep of set plaster of Paris, with the aim to identify the underlying mechanisms and to estimate their applicability to the cementitious materials. Indeed the elimination, or at least limitation, of this drawback requires the understanding of its microscopic origin. Few studies have been devoted to the investigation of the link between the microstructure and the mechanical properties of set plaster. Concerning the influence of water, the few existing studies have brought some clues for the interpretation of the stiffness and resistance of set plaster in humid or wet environments. But up to now, the creep in presence of water had not re-

ceived any explanation. We have proposed recently that it derives from the dissolution of gypsum [1]. This finding has enabled to propose pressure solution creep as the mechanism of wet creep of set plaster. We detail here the experiments (mechanical tests and interferometric measurements) leading to this result and discuss its implications for hydrated Portland cement.

2. Mechanical properties of gypsum plaster in presence of water

Set plaster is constituted of intricate gypsum ($CaSO_4, 2\,H_2O$) needles, roughly 20 μm long, obtained from the hydration of plaster of Paris ($CaSO_4, \frac{1}{2}\,H_2O$). The cohesion of the material derives from the bonds between the needles and from the tenon and mortise joints between them [2]. It has been postulated about ten years ago that the bond between the needles is of the same nature as the bond between flocculated colloids [3]. Therefore the gypsum microcrystallites should be linked via a nanometric water film. The attraction between them should stem from van der Waals interactions between the facing charged faces and ionic correlations between the Debye layers developing in the water close to the surface, and the repulsion from the exclusion of the Debye layers. At the ends of the water layers, capillary forces develop at menisci and contribute to the cohesion between the needles. The balance between these forces determines the liquid film thickness. It has been added a few years later that the presence of "bridging", i.e., solid, interfaces, beside these "non-bridging" liquid interfaces between needles, is necessary to obtain a more comprehensive interpretation of the set plaster properties [4]. This vision of the microstructure of the material enables to interpret several mechanical properties of wet or humid set plaster:

- it has been observed that Young's modulus of set plaster decreases when the relative humidity increases [5, 6]. This can be interpreted by the fact that the equilibrium thickness of the water inter-needle layers increases with the relative humidity enhancement, from ~ 1 nm in dry conditions to ~ 10 nm in humid ones [3]. And a thicker layer induces a weaker bond between needles. The assumption has been made that this weakened connection can result in a reversible slip between some microcrystallites, increasing the elastic strain, thus decreasing Young's modulus. The bridging bonds deform only by elastic bending and guarantee that no irreversible strain occurs.

- The flexural strength, i.e., the bending failure stress of this brittle material, has also been seen as decreasing when the material is soaked in water [7] or when it adsorbs water [8]. This feature can also be ascribed to the thickening of the water layers in a humid environment. Indeed the resulting slip between microcrystallites implies a lower contribution of the non-bridging bonds to the strength, so a lowered failure stress.

- It has also been observed that, if the hardness of a set plaster sample decreases after being plunged in water, the hardness recovers its initial value once the sample is dried [7]. The reversibility of the influence of water can again been interpreted by the fact that the mechanical resistance of the material reflects the values of the inter-needle water slab thickness, in equilibrium with the quantity of water available. If more water is available, the layer thickens and the cohesion diminishes, and vice-versa.

3. Wet creep of gypsum plaster

Beside these successes of the theory, one should mention that unfortunately it does not provide any mean to understand the increase of creep in a humid environment [9, 10]. Indeed creep is a slow process occurring over periods of days or months, whereas the equilibration of the intercrystalline water layers is a quasi-instantaneous mechanism. Thereby the progressive plastic strain occurring during creep cannot be explained by a progressive increase of the slab dimension leading to a loss of cohesion.

We show here that the wet creep of set plaster is a consequence of a phenomenon called pressure solution creep (figure 1). When an external stress, or simply its own weight, is applied to a gypsum board, the gypsum needles are subject to local stresses. These stresses induce an increase of the chemical potential of the gypsum. So when water is present, in particular in the intercrystalline contacts, to recover chemical equilibrium, the chemical potential of the liquid increases also to equalize with the one of the solid. This leads to the enhancement of the solubility of gypsum, thereby to a dissolution of the solid in the liquid. Therefore concentration gradients appear along the water layers, which induce Fick diffusion of dissolved gypsum. When the sulfate and calcium ions reach areas without stress, their solubility recovers its initial value and they precipitate on the solid at rest. This dissolution-diffusion-precipitation series continues as long as the local stress exists, and induces a transfer of matter from high stress to low stress regions. By this way a plastic strain occurs, which accommodates the applied stress, and the material creeps.

This phenomenon is well known in geology. It has been ascribed several

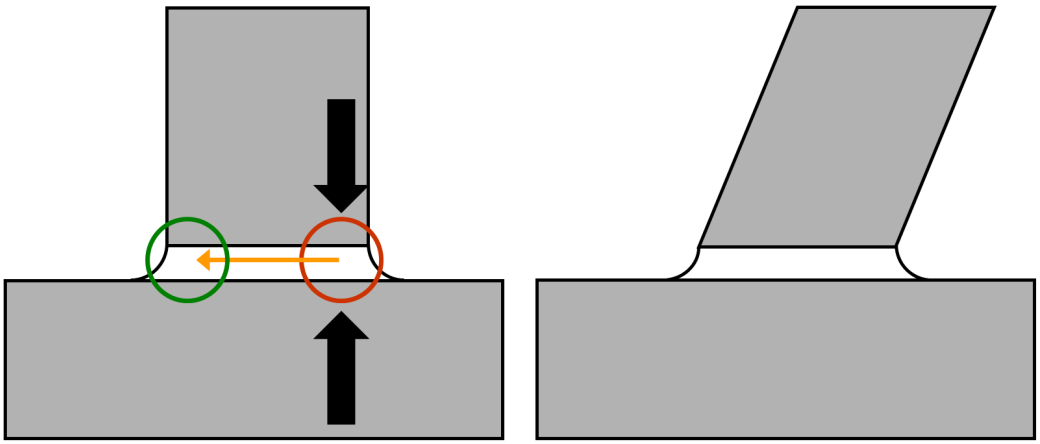

Figure 1: Sketch of the consecutive steps of pressure solution creep in gypsum plaster: an external load creates a local compression stress between two gypsum needles, which induces dissolution, diffusion of the dissolved species, and recrystallisation in a non-stressed area. This sequence induces a local transfer of matter, so a macroscopic plastic strain.

contributions to the upper crust evolution, for instance during non-seismic strain of active faults, or for the transformation of loose sediments into cohesive sedimentary rocks [11]. Pressure solution creep has in particular be evidenced in wet gypsum particulates under uniaxial and hydrostatical load [12, 13].

Numerous experiments of pressure solution creep in water have been performed in laboratory, with the final aim of understanding geological situations. Many of these studies use model systems or model configurations from which we can learn on the basic mechanisms and characteristic kinetics of pressure solution [11]. But their specific features, generally devoted to geology, make their application to industrial materials difficult. For instance, the available works on pressure solution in gypsum study low porosity assemblies

of non-cohesive quasi-spherical gypsum crystallites,. All of these characteristics differ from industrial gypsum, thereby making the application of these studies difficult to building materials. We have not found such a study in the materials science field. Therefore a protocol enabling to validate the existence of pressure solution in the creep of humid gypsum plaster is necessary.

Before going on, we would like to recall that it was formerly thought that the decrease of the mechanical strength of set plaster with moisture could be due to the dissolution of small gypsum crystals, precipitated at the end of the plaster setting and bridging the gypsum needles [14, 15]. This phenomenon was sometimes misleadingly called "dissolution-recrystallization". Pressure solution creep mentioned here also involves dissolution and recrystallization but in a totally different way: dissolution occurs at high stress regions of inter-needle contacts and recrystallization at low stress regions or at the needles surface. No microcrystal appears or disappears. This hypothesis of dissolving-recrystallizing microcrystals was unambiguously discarded by hardness and bending tests in various conditions of plaster setting and relative humidity [7].

To establish a protocol of validation of the presence of pressure solution creep, we benefit from the methodology of the works performed on the geological side. In these studies, the presence of pressure solution creep, and its exact nature, is usually determined by measuring the creep kinetics. The slowest step in the reaction-transport-recrystallization sequence limits the matter transfer rate, so drives the whole kinetics and determines the evolution laws.

The theoretical determination of the exact expression of $\varepsilon(t)$, the strain

evolution with time, requires to define precisely many parameters: order of the chemical reaction, reactive surface area, thickness of the liquid slab, locus of the precipitation sites, porosity, size distribution of the mineral grains, width of the solid contacts, ... The final $\varepsilon(t)$ curves have been found to be highly dependent on the above characteristics of the system and on their interplay. A particularly complete modelization of pressure solution creep in sandstone for instance can be found in Ref. [16].

As no complete pressure solution modelization of a highly porous medium like set plaster exists, we have to make with first-order models, bringing at least trends of the strain evolution with time. We have chosen the acclaimed model of Raj [17]. His modelization considers the creep of a unique stressed cubic mineral sample in a solvent present in channels at its surface. It states that :

- if the kinetics is driven by the mass transport (due in general to a low flow rate of diffusion in tiny channels), the strain rate writes:

$$\mathrm{d}\varepsilon/\mathrm{d}t \sim \sigma D\, s/d^3 \tag{1}$$

- if the kinetics is driven by the surface reaction (due to its slowness), the strain rate writes:

$$\mathrm{d}\varepsilon/\mathrm{d}t \sim \sigma k\, s/d \tag{2}$$

In these expressions, σ is the applied stress, D the diffusion coefficient of the dissolved species, k the reaction rate constant of the mineral, s its solubility and d the characteristic size of the constrained interface.

In geological laboratory experiments, the limiting step is estimated in varying the grain size d and determining if the strain rate scales as d^{-1}

or d^{-3}. In our case, varying the gypsum crystallites size in set plaster is difficult. To identify the limiting stage, we have benefited from the existence of admixtures added to the plaster industrially to limit the humid creep. These additives are efficient in slowing down the creep strain rate, but again, their mechanism of action is not understood yet. So the idea of our work is to find which factor of the above expressions, if any, these admixtures modify, to lower the strain rate, thus indicating the working mechanism of creep.

4. Experiments

In equations 1 and 2, the parameters the knowledge of which is needed are d, s, k, D and $\mathrm{d}\varepsilon/\mathrm{d}t$.

4.1. Admixtures

The investigated anti-creep admixtures are a tartaric acid ($C_4H_6O_6$) / boric acid (H_3BO_3) mixture, Trilon P, i.e., a commercial version of a sodium salt of a polyamino carboxylic acid ($C_{10}H_{16}N_2O_8$, CAS no. 454473-50-8), Sequion 50K33 and Dequest 2054, i.e., two commercial versions of the hexamethylene-diamine tetra(methylene phosphonic acid) hexapotassium salt ($C_{10}H_{22}K_6N_2O_{12}P_4$, CAS no. 38820-59-6), and STMP, i.e., sodium trimetaphosphate ($Na_3P_3O_9$). The acid mixture is made of 1/6 of tartaric acid and 5/6 of boric acid in weight.

4.2. Bend creep tests

For the bend tests, gypsum (from Mazan quarry, France) is ground and dehydrated to make plaster ($CaSO_4$, $\frac{1}{2}H_2O$). The resultant powder is mixed with water to make a paste with a water/plaster weight ratio of 0.8, bringing

a convenient compromise between the fluidity of the paste and the porosity of the final product (57%). The mixture is cast in a parallelepipedic mold, placed in a closed vessel during 24 h to achieve complete hydration, dried, and stored in calcium sulfate saturated water until the test, to avoid dehydration [15]. The same protocol was also followed with water containing the various admixtures.

Standard bend tests have been performed to measure the creep strain rate of set plaster. The above-described samples were loaded in the middle on the top face and supported at their ends. The deflection was recorded with a Linear Variable Differential Transformer displacement sensor every 2 h during 15 days. During the tests, the beams were immersed in water —to study wet behavior— saturated with calcium sulfate —to avoid normal dissolution and be sure to observe, if any, pressure dissolution. The maximum load was chosen as 20% of the tensile strength, measured for each batch on one sample before the test, to remain outside the stress range where subcritical crack growth inside the samples is expected, risking to blur the results [9, 18].

The force and displacement are converted in the stress σ and strain ε at the top face in the middle of the beam with the elastic approximation:

$$\sigma = \frac{3PL}{2wh^2} \quad \text{and} \quad \varepsilon = \frac{6h\delta}{L^2} \tag{3}$$

In these expressions, P is the load, L the support span, $w = 20$ mm the width of the beam and $h = 20$ mm its height.

The zero-stress curve inside the beam may depart from the center of the beam, due to non-symmetry of the compressive and tensile strain mechanism, which may make these formulas non valid. But the determination of the exact stress field is not possible and would deserve a study for itself.

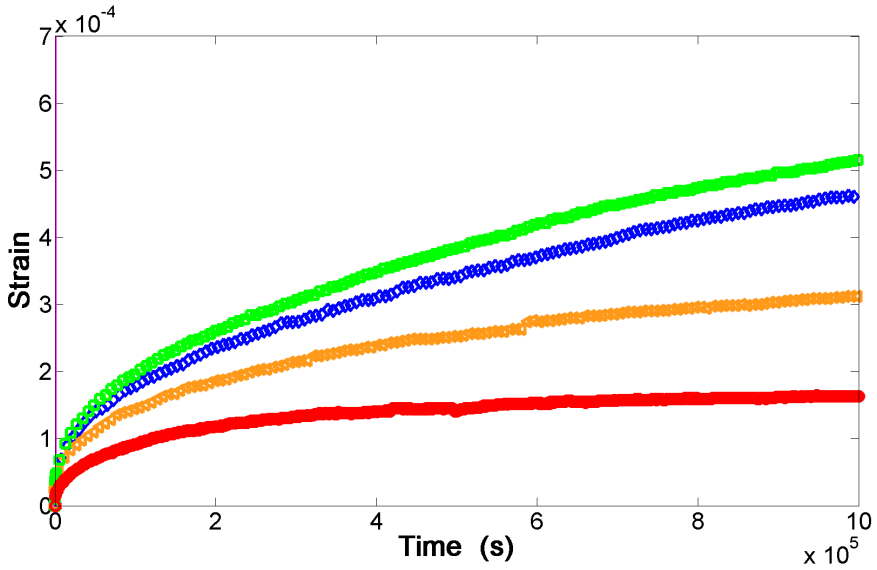

Figure 2: Evolution with time of the bending strain for the gypsum plaster samples manufactured with 0.15% Sequion in the preparation water. The applied stress, from the bottom to the top curve is 0.244 (red), 0.332 (orange), 0.356 (blue) and 0.386 (green) MPa.

An example of $\varepsilon(t)$ curves at various stresses for one admixture is shown in figure 2. The strain rate $\mathrm{d}\varepsilon(t)/\mathrm{d}t$, needed for the test of the above-mentioned equations is obtained in derivating the experimental $\varepsilon(t)$ curves numerically. From it, the creep compliance rate $(\mathrm{d}\varepsilon(t)/\mathrm{d}t)/\sigma$ is computed. All strain-time data and curves for all admixtures and stresses can be found as Supplementary Material.

A parameter that may play a role in the elaboration of the samples is the concentration of admixture in the water used to manufacture the gypsum from the plaster powder. Several concentrations between 0.05% and 0.5% in weight have been tested for each additive. The creep results have been found to be independent on the concentration, except for the smallest

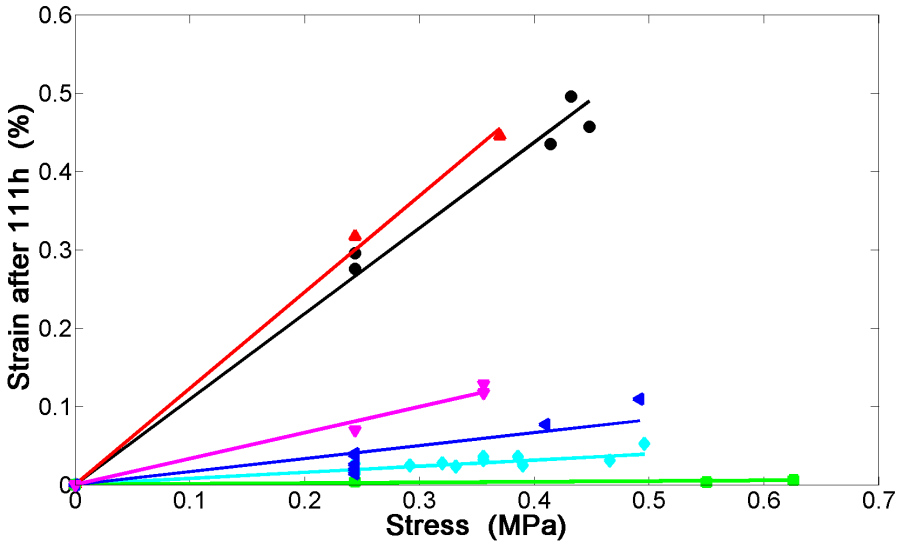

Figure 3: Bend strain ε after 111 h versus applied stress σ for the various admixtures: pure water (black circles), boric/tartaric acid (red upward triangles), Trilon (pink downward triangles), Dequest (blue leftward triangles), Sequion (light blue diamonds), STMP (green squares).

concentrations ($\lesssim$0.1%) where the anti-creep action is less efficient.

The strain obviously depends on the bending stress. To get an estimate of the evolution of the creep intensity with the applied stress, the value of the bend strain at one given time (namely 111h) has been drawn versus the bend stress in figure 3. It can be stated that the creep is roughly proportional to the applied stress in the range investigated in this study.

4.3. Contact size

The determination of the inter-needle contact size d is not a trivial task and for this we have performed scanning electron microscopy observations of the microstructure of the set plaster samples (figure 4). For all the admix-

tures used, the microstructure remains of the acicular type. None of them reveal lenticular or columnar habit, sometimes encountered in natural gypsum, depending on the impurities adsorbing on specific crystalline planes. The characteristic size of the microcrystals is similar at first order in all pictures and we have considered that the contact size d should also be similar among all samples. For the computations in next section, the average value of $d = 1\,\mu$m has been chosen.

Nevertheless we can mention that gypsum plaster elaborated with Sequion reveals unexplained micrometer-size etch pits at the needles surface. Whereas we have seen that, according to the SEM pictures, the influence of the additives on the set plaster microstructure is not significant, we have attempted to get a further evidence of this lack of influence in testing another protocol of elaboration of the samples. In this process, all solid samples are first elaborated from plaster and pure water, in the absence of any admixture. Subsequently, each sample is soaked during 12h in water containing a given concentration of additive, to make the molecules impregnate the gypsum crystallites network of the material. The creep bend tests are then performed as detailed in section 4.2. The interest of this procedure is to guarantee that all samples have strictly the same microstructure, having all been elaborated in pure water.

Figure 5 shows the creep curves for one admixture present in the impregnation water at various concentrations. As the applied stresses are almost similar, the difference between the various curves can be ascribed to the concentration of additive in the soaking water. The more concentrated in additive the impregnation solution, the more efficient the anti-creep effect. The

origin of this evolution is to be searched in the variation of the dynamics of adsorption and diffusion in a porous medium of the admixture for the various concentrations. This result seems to indicate that the quantity of molecules inside the sample is not the same for the various concentrations, even with the long impregnation time we have chosen. The adsorption and diffusion dynamics may be different from one admixture to another, which makes the comparison between the results obtained with the various additives quite delicate. Therefore, we have abandoned this process and exclusively used the protocol presented in the previous section, where we have the certainty that the molecules are embedded in the samples.

4.4. Solubility

The solubility of gypsum in aqueous solutions of the various admixtures has been determined by induced coupled plasma atomic emission spectroscopy. Certainly due to the low concentration of additive here, no departure from the solubility of gypsum in pure water (2 g/L, 15 mmol/L) has been found, whatever the added product.

4.5. Dissolution rate constant

The gypsum-water interfacial reaction rate constant is also needed, being either the dissolution or precipitation rate constant in Raj's equation. De Meer and Spiers identified precipitation as the driving mechanism, which can be expected in their low porosity system, where unstressed precipitation sites are rare [13]. But the dissolution and precipitation rate constants should be close. Indeed the rate of attachment and detachment of ions at a solid surface are strongly linked, and a change of the surface reactivity influence

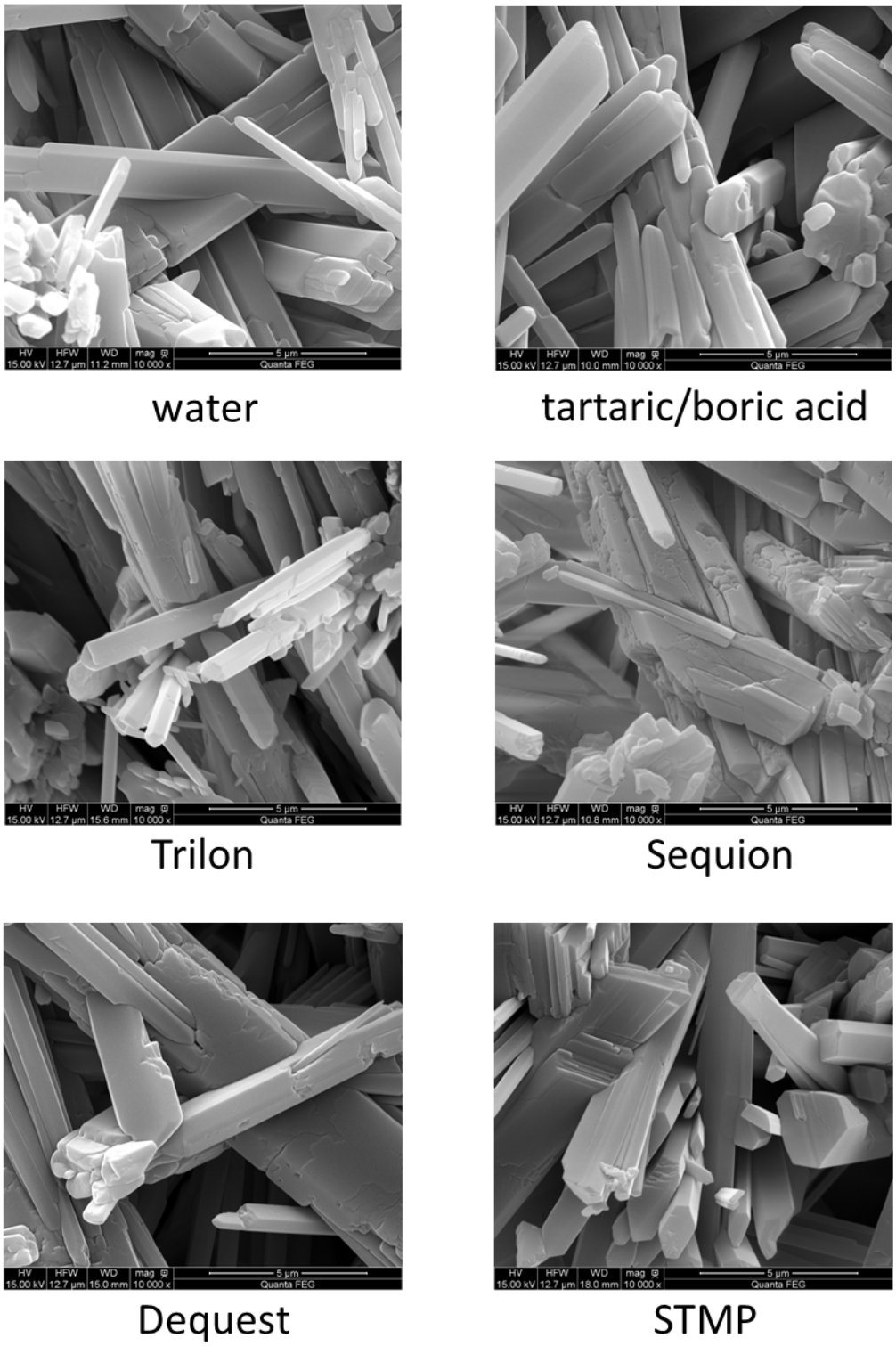

Figure 4: Scanning electron microscope pictures of set plaster samples, pure and elaborated with the various admixtures. The dimension of the images is $12.7 \times 11.0\,\mu\mathrm{m}^2$.

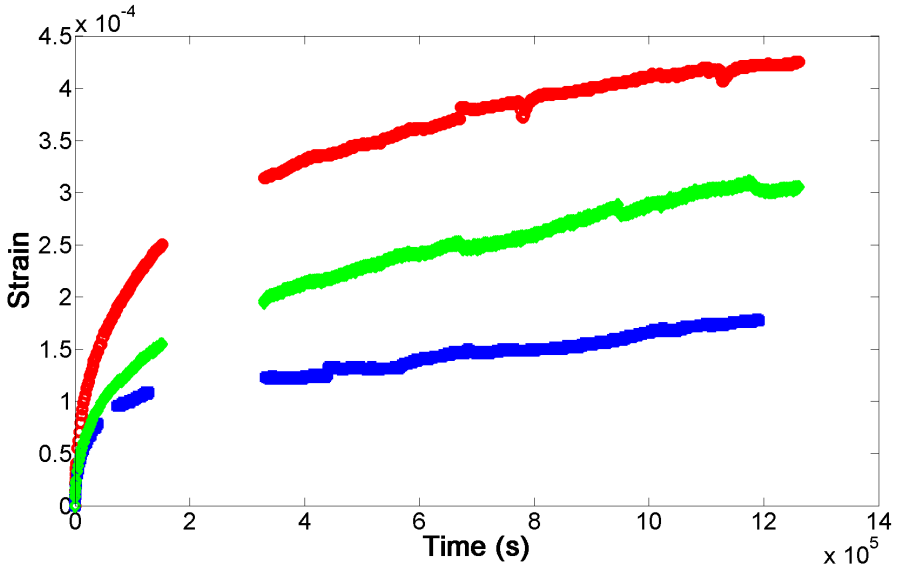

Figure 5: Evolution with time of the bending strain for the pure gypsum plaster samples impregnated by Sequion. From the top to the bottom curve, the concentration of Sequion in the impregnation water is 0.50 g/L for a 0.406 MPa stress (red), 4.97 g/L for a 0.524 MPa stress (green) and 9.94 g/L for a 0.496 MPa (blue).

both [19]. We have chosen to study the dissolution rate constant. But if a correlation between creep and dissolution is found and shows that the phenomenon is interface-driven, it is very likely that a correlation between creep and precipitation also exists.

The measurement of the dissolution rate constant is a delicate task. As we have shown in preceding studies, the usual solution chemistry methods provide dissolution rates blurred by mass transport phenomena (diffusion, convection) [20, 21]. As the possible effect of admixture on the dissolution rate constant may be tiny, the standard dissolution measurement techniques were not appropriate and we have used an alternative methodology, holographic interferometry. This technique has been described in detail in Ref. [22]. It presents two major advantages. First the experiment is performed in quiescent water, thereby avoiding any convective disturbance. Secondly the concentration is directly measured at the solid-liquid interface, whereas in standard methods it is measured in the flowing liquid far from the surface.

The dissolution rate constant k of gypsum of the same origin as in the bend tests —to allow comparison— in water containing the various admixtures has been measured by holographic interferometry and for all of them, k has been found to be modified by the admixture [23]. The results are summarized in table 1.

4.6. Diffusion coefficient

The holographic interferometry experiments have also the advantage to give access to the diffusion coefficient D of dissolved gypsum in water. Therefore D has been measured for gypsum in water containing the various admixtures and it has been seen that this coefficient is almost constant for all

Admixture	k (10^{-6} mol m^{-2} s^{-1})	D (10^{-10} m^2 s^{-1})
Without	46	7.1
Tartaric-boric acid	74	5.9
Trilon	21	4.3
Sequion	11	6.1
Dequest	8.0	4.9
STMP	3.3	6.5

Table 1: Dissolution rate constant k and diffusion coefficient D of gypsum in water containing various admixtures, measured by holographic interferometry.

admixtures, probably due to the low concentration of the products, as shown in table 1.

5. Results and discussion

Before testing our assumption of pressure solution creep using all the experiments described in the preceding section, we would like to focus first on the $\varepsilon(t)$ curves. They constitute the first systematic study of the wet creep of gypsum plaster. By fitting the curves, we have noticed that all of them obey to a power law: $\varepsilon(t) = At^n$, with $n < 1$. Thereby, we see that a consolidating mechanism is active during the wet creep, which slows down progressively the strain. The creep exponent n depends on the admixture with which the set plaster sample has been manufactured: 0.69 for pure water, 0.71 for boric/tartaric acid, 0.52 for Trilon, 0.34 for Sequion, 0.39 for Dequest and 0.38 for STMP. It is striking to state that it evolves from $\sim$2/3 to $\sim$1/3 from pure water to the most efficient anti-creep admixture. Figure 6 illustrates this evolution. We have not found yet the origin of this ability

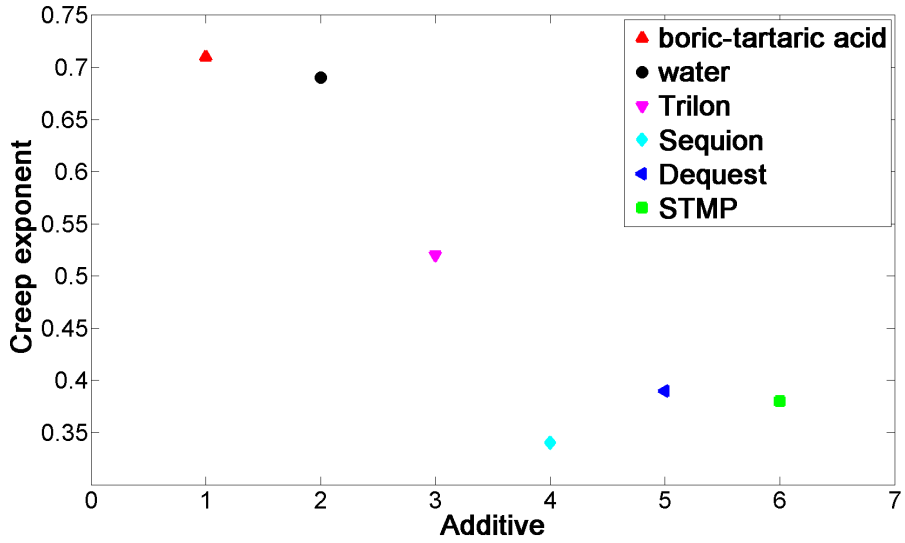

Figure 6: Bend creep exponent of wet gypsum plaster manufactured with the various admixtures.

of admixtures to lower the creep exponent. We can just mention that the 1/3 exponent in presence of anti-creep products recalls both i) the exponent of Andrade creep, i.e., diffusive creep in non-porous materials, and ii) the pressure solution creep exponent observed in NaCl single crystals by Dysthe et al. [24].

We are now able to test the agreement between our experiments and equations 1 and 2. For the first one, we have plotted in figure 7 the creep compliance rate $\dot{\varepsilon}(t_0)/\sigma$ as a function of $D\,s/d^3$. To gain statistical accuracy, each dot in this figure represents an average of the results of a few experiments performed at quasi-equal stresses. The question of the choice of t_0 arises. Indeed the $\varepsilon(t)$ curves are non linear. We have chosen $t_0 = 1 \times 10^5$ s, in the middle of the investigated time, but we have checked otherwise that the

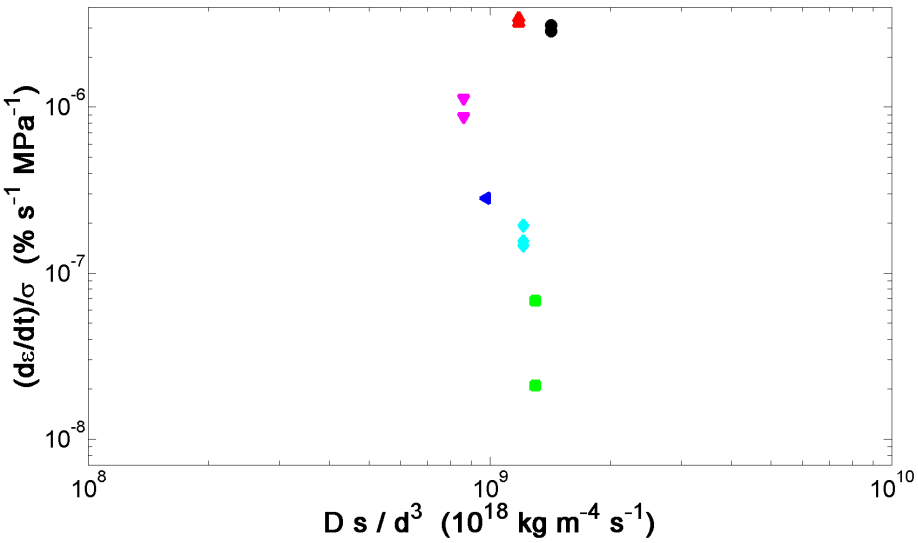

Figure 7: Compliance rate for wet bending creep of gypsum plaster elaborated with a given additive at $t_0 = 1 \times 10^5$ s, as a function of a coefficient proportional to the diffusion coefficient of dissolved gypsum in a solution of the same additive. Red upward-pointing triangles: tartaric/boric acid; black circles: pure water; pink downward-pointing triangles: Trilon; blue left-pointing triangles: Sequion; light blue diamonds: Dequest; green squares: STMP.

obtained correlation is valid all along the experiments. As can be seen in figure 7, no correlation is observable between the 2 factors. The compliance rate varies of 2 orders of magnitude among the admixtures, whereas the diffusion coefficient remains almost constant (s and d keeping always the same value). Therefore the diffusion velocity of the gypsum dissolved species has no influence on the creep kinetics, which discards the diffusion-driven pressure solution creep as creep mechanism.

Now, to test equation 2, we have drawn in figure 8 the creep compliance rate $\dot{\varepsilon}(t_0)/\sigma$ as a function of $k\,s/d$. Again, each dot in the figure stands for an

average of the results of a few experiments performed at close stresses. Here we see a very strong correlation between the two quantities. Indeed $\dot{\varepsilon}(t_0)$ and k evolve of almost 2 orders of magnitude from pure water to the most efficient anti-creep coefficient, giving rise to the observed coupling between the two parameters in figure 8. This correlation is a strong support to the fact that the wet creep of gypsum plaster is a reaction-driven pressure solution creep. Again the correlation is shown at $t_0 = 1 \times 10^5$ s in figure 8 but we have checked that the correlation exists all along the experiments. If the link between dissolution velocity and creep velocity is established, we have to mention that the first order model of the phenomenon we have used (in absence of a more complete model) does not catch the exact correlation. The model predicts $\dot{\varepsilon} \sim (\sigma k s/d)^m$ with $m = 1$ and we find $m = 1.3$ to 1.7, slightly evolving between the beginning and the end of the experiment.

We would like to mention here the compressive creep tests performed by Hoxha et al. with natural gypsum rocks [25]. They mention that the duration of their experiments is too short ($\sim$ 15 days) to evidence pressure solution. Therefore they explain the expansion of their samples by a mechanism of reversible migration of water molecules, from the solid to the pore space. As shown here, the consequence of pressure solution creep may be observable even for such short period of time. With the material at hand, we are not able to explain why they do not observe precipitation-limited pressure solution creep like de Meer & Spiers with a system of similar porosity [13].

Now that the basic mechanism of the wet creep of gypsum plaster is elucidated, a detailed theoretical analysis of pressure solution in an as porous material as gypsum plaster would enable to make quantitative predictions

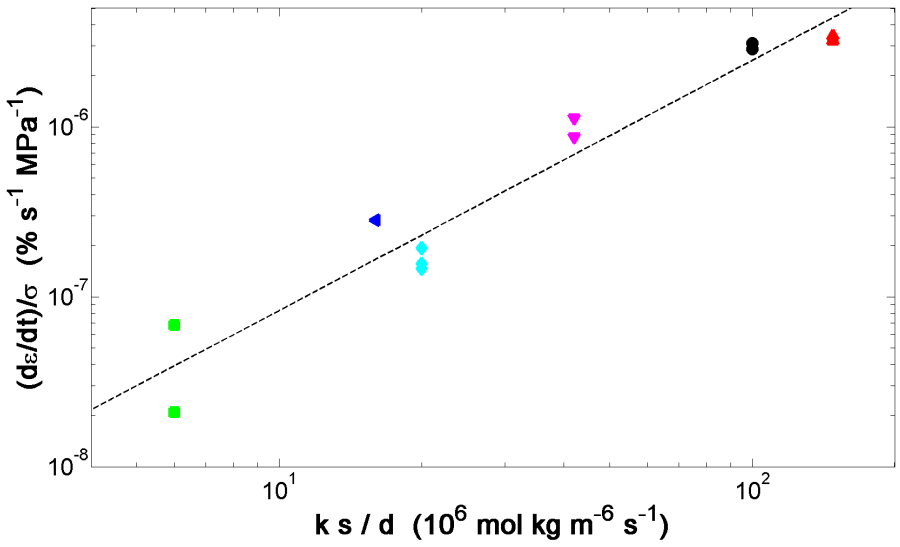

Figure 8: Compliance rate for wet bending creep of gypsum plaster elaborated with a given additive at $t_0 = 1 \times 10^5$ s, as a function of a coefficient proportional to the dissolution rate constant of gypsum in a solution of the same additive. The color code is the same as in figure 7. The black dashed line is a linear fit of the data.

about its kinetics. But knowing that the dissolution kinetics is at the basis of wet creep enables to try to find tools against this drawback of the material.

6. Implications for hydrated Portland cement

Despite being the manufactured material most used on earth, the structure and cohesion of hydrated Portland cement is not perfectly understood yet. Along a schematic view, a hydrated Portland cement paste can be considered as a floculated colloidal suspension of calcium-silicate-hydrate (C-S-H), i.e., $(CaO)_{1.7}(SiO_2)(H_2O)_{1.8}$ [26], nanometric particles, called gel, with partial crystallinity [27]. $Ca(OH)_2$ nanocrystallites, and other minor hydration products, are also present in the gel. Like in standard colloidal gels, the remarkable strength of this hydraulic cement stems from electrostatic and ionic correlation forces between the particles via the water layers between them [28]. Capillary forces contribute also in unsaturated materials, where water-air menisci are present.

It is generally admitted that C-S-H is found in hydrated pastes in 2 or 3 forms, of identical chemical composition, but clearly distinct organizations and densities [3, 29, 30]. The proportion of these phases varies with the water/cement ratio used to manufacture the cement paste, the drying, and the aging of the material. This structural heterogeneity induces a multi-scale porosity, also evolving with the just-mentioned parameters.

One major concern about cementitious materials is their aging, in the form of shrinkage, creep, fractures, ... partly due to the slow drying of the products of cement hydration [31]. It has been shown that the concrete creep strain results exclusively from the irreversible strain of the cement hydration

products [32] and the creep of hardened cement is still an active field of research [30].

We discuss here only about wet creep, i.e., the plastic strain under small load of the water saturated material. In these conditions, capillary menisci inside the material are absent, which suppresses a major source of aging of the material. Therefore in this case the creep cannot derive from shrinkage induced by water loss, and corresponding models do not apply [31]. Recent assumptions of creep origin applying in this situation are: reorganization of high density phase globules, analog to dislocation migration in crystals [29], reorganization of C-S-H particles, leading to an increase of the packing factor of the 3 phases, analog to granular matter flow [30], better alignment of C-S-H sheets, analog to house-of-card collapse [32], ...

All of these hypotheses rely on the sliding of C-S-H nanoparticles, or of C-S-H sheets, enabling reorganization [33]. An alternative proposal, beside sliding, has also been made to explain the relative motion of C-S-H particles. The possibility of the existence of the dissolution-diffusion-recrystallisation series, leading to a transfer of matter among the C-S-H particles, inducing plastic strain, has also been proposed [3]. Theoretical predictions of hydrating concrete creep have even been proposed [34, 35]. But these analytic laws are phenomenological and postulate a priori the existence of a significant influence of the applied stress on the dissolution of the hardened material. We have shown here that this influence is significant and measurable in the case of wet gypsum and want to discuss here the case of hydrated cement.

Hydrated cement pastes share common characteristics with gypsum plaster: They both simultaneously shrink and harden during drying, they swell

when immersed in water after setting, and they experience humid creep. The question of the existence of pressure solution in saturated hardened cement arises. As for gypsum, a direct observation is not possible for the moment and correlations have to be sought. Recent C-S-H nanoindentation measurements have shown a logarithmic creep [30]. As no comprehensive model of pressure solution creep exists, it is unfortunately not possible to draw any conclusion about pressure solution from this lograrithmic evolution of the strain [11]. The order of magnitude of the creep compliance rate in these experiments evolves from 10^{-9} to 10^{-10} $\%\,\mathrm{s}^{-1}\,\mathrm{MPa}^{-1}$, for samples ages similar to ours ($\sim$ 10 days). In our experiments with gypsum plaster, its values is about 10^{-6} $\%\,\mathrm{s}^{-1}\,\mathrm{MPa}^{-1}$ (figure 8).

The crystallites in C-S-H are nanometric. The inter-particle contact length is therefore of the same order of magnitude or lower, so 3 orders of magnitude smaller than in set plaster, where it is micrometric (figure 4). Therefore if pressure solution plays a role, the mass transport time between particles should be negligible and the phenomenon should be reaction-driven, as in the case of gypsum, and depend on the dissolution rate constant of the material via equation 2.

Making the first order assumption that the correlation in gypsum plaster and hydrated cement pastes are similar, we should have $(\dot{\varepsilon}/\sigma)_{\mathrm{C-S-H}}/(\dot{\varepsilon}/\sigma)_{\mathrm{gypsum}} \sim (ks/d)_{\mathrm{C-S-H}}/(ks/d)_{\mathrm{gypsum}}$. Let us review the parameters in this equation. The solubilities of the hydrated phases of cement depend highly on the nature and structure of the phase and on the chemical environment. But the order of magnitude of the solubility of calcium has been measured as 10 mmol/L, comparable to the 15 mmol/L solubility of calcium in the case of

gypsum [36]. The creep compliance rate $\dot{\varepsilon}/\sigma$ of hardened cement mentioned above are 3 orders of magnitude lower than the one of gypsum plaster. The characteristic size d of the interface between C-S-H particles is also 3 orders of magnitude lower than in gypsum plaster.

Therefore, a dissolution rate constant of $k_{\mathrm{C-S-H}} \sim 10^{-6}\, k_{\mathrm{gypsum}} \sim 10^{-11}$ $\mathrm{mol\,m^{-2}\,s^{-1}}$ would enable to explain the change in the nanoparticle structure responsible for the creep observed in the experiments of Vandamme & Ulm [30]. Measurements with radiotracers of the dissolution rate of C-S-H suspensions in aqueous solutions have brought a value $k_{\mathrm{C-S-H}} \sim 3 \times 10^{-12}$ $\mathrm{mol\,m^{-2}\,s^{-1}}$ [37]. This value is of the same order of magnitude as the value we think necessary to make pressure solution active during C-S-H creep. Therefore this order of magnitude analysis brings pressure solution among the possible phenomena acting in the creep of C-S-H.

We would like to stress on the fact that our assumption is consistent with all the creep models mentioned above. The novelty does not lie in the geometry of the motion of the nanoparticles, but in the way of this motion, dissolution-recrystallisation instead of sliding. To strengthen this hypothesis, the measurement of the dissolution rate constant of C-S-H, and other hydrated phases, in aqueous solutions representative of the liquid present in the nanopores of hardened cement are highly desirable, essential to base on experimental evidence the contribution of pressure solution to concrete creep. Besides, if the role of dissolution is corroborated, its exact role on the creep strain will have to be specified. For instance, whether the dissolution-diffusion-precipitation sequence results in a creep strain accomodating the stress like in gypsum plaster [3], or the dissolution induces a thinning of the

crystallites inducing a viscoelastic strain progressively increasing with time [35], will have to be clarified.

7. Conclusion

We have performed wet bending creep tests to measure the strain rate of set plaster manufactured with various anti-creep admixtures (boric/tartaric acid, Trilon, Sequion, Dequest, STMP). Besides we have carried out holographic interferometry experiments to measure the dissolution rate constant of gypsum in water containing these anti-creep admixtures, and the diffusion coefficient of dissolved gypsum in these solutions. A strong correlation has been found between the wet creep strain rate and the dissolution rate constant of the material. This clear dissolution-creep link has enabled to propose reaction-driven pressure solution creep as the underlying mechanism of the wet creep of gypsum plaster. This is the first time that this phenomenon is evidenced experimentally in an industrial material.

Following the study of gypsum plaster, an order of magnitude analysis has shown that pressure solution may also contribute to the creep of hydrated Portland cement. Indeed, alternatively to the sliding between the hydrated phase nanoparticles, the dissolution-diffusion-recrystallization sequence was shown to be another mean of the reorganization of the nanoparticles during creep.

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