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Jean Colombani, M. Bellotto. Optimization of Anti-creep Admixtures for Plasterboards. Ninth International Conference on Creep, Shrinkage, and Durability Mechanics (CONCREEP-9), Sep 2013, Cambridge, MA, United States. pp.380-387, 10.1061/9780784413111.045 . hal-03789740

HAL Id: hal-03789740

<https://hal.science/hal-03789740>

Submitted on 27 Sep 2022

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Optimization of Anti-creep Admixtures for Plasterboards

J. Colombani¹ and M. Bellotto²

¹Institut Lumière Matière, Université de Lyon, Université Claude Bernard Lyon 1, CNRS UMR5306, campus de la Doua, F-69622 Villeurbanne, France; PH (+33) 4 72 44 85 70; FAX (+33) 4 72 43 26 48; email: jean.colombani@univ-lyon1.fr

²Giovanni Bozzetto S.p.A., via Provinciale, 12, I-24040 Filago (BG), Italy; email: maurizio.bellotto@bozzetto.it

ABSTRACT

We have measured by digital holographic interferometry the dissolution rate constant of gypsum in water containing various phosphonates, both small molecules and polymers, known to adsorb at the gypsum crystal surface. We have beside measured by rheometry the shear creep rate of gypsum plaster containing these phosphonates in saturated humid environment. The phosphonates decrease both the dissolution velocity and humid creep velocity, consolidating the assumption of reaction-driven pressure solution creep for the humid creep of gypsum plaster. All these phosphonates are efficient anti-creep admixtures of humid set plaster, the polymeric ones having the complementary advantage to be easier to use, with a less delicate dosage.

INTRODUCTION

Plasterboard is a universally employed building material. It is a cheap, light, insulating and fireproof solid, which compensates for its weak mechanical strength. One striking example is the enhancement of the creep of set plaster by a humid environment. It constitutes a strong limitation of the durability of this material, especially in regions with a humid climate.

It has been recently demonstrated that the creep strain rate of wet set plaster is driven by the water dissolution kinetics of gypsum (Pachon-Rodriguez et al., 2011). This knowledge has enabled us to propose a model for the creep mechanism (reaction-driven pressure solution creep) and to give elements to improve the humid gypsum plaster long-term mechanical behavior. Indeed the dissolution properties of gypsum are modified by the presence of foreign ions in the solution which adsorb at the surface and thus, according to the model, should modify the creep rate of the material. Phosphate and phosphonate salts are known to be effective crystal growth modifiers for calcium containing crystals, affecting dissolution as well as growth (Liu and Nancollas, 1973), therefore being likely to slow down humid creep of polycrystalline gypsum.

To identify new potential anti-creep admixtures in this product family, we measure in this work the dissolution rate constant, relevant for quantifying the reaction kinetics, of gypsum in aqueous solutions of different phosphonates, both of

simple molecular structure and of polymeric nature. As the variation of the dissolution rate constant among these products may be tiny, a non-standard experiment (holographic interferometry) has been used for the measurements. This convection-free technique gives access with unprecedented accuracy and precision to the dissolution rate constants (Pachon-Rodriguez, 2013).

The anti-creep performance of these admixtures is then tested by recording the strain evolution vs. time of samples of set plaster submitted to a constant stress under water vapor saturated conditions in a rheometer. The anti-creep efficiency is obtained by comparison with the creep curves of set plaster produced without admixtures. These experiments have led to the confirmation of our assumption on the origin of the wet creep, and to the finding of new anti-creep admixtures. In addition, via the dosage of the admixture, it has been evidenced the importance of the texture of the polycrystalline material on creep rate.

CHOICE OF ANTI-CREEP ADMIXTURES FOR GYPSUM PLASTER

Set plaster is made of intricate micrometer-size gypsum needles ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), obtained from the hydration of plaster, i.e., calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$). Adjacent crystallites are considered to be linked either via a solid junction, or via a thin water film. In water, the nanometric thickness of this water slab stems from the balance between the dispersive attraction between the crystallites and the repulsion of the Debye layers present in the liquid film close to the surfaces, as in flocculated colloids (Chappuis, 1999; Gartner, 2009). In a humid atmosphere, capillary forces at the liquid film extremities contribute also to the attraction between needles and increase the stiffness and strength of the material.

If the water layer thickens (due to the increase in relative humidity or the material soaking in water) the intercrystalline interaction is weaker and gypsum needles may slide. Various mechanical properties of set plaster in the presence of water can find explanation in this behavior (fall of rigidity, compressive strength, and bending strength, reversibility of hardness decrease induced by the material wetting).

But the equilibration of the water film thickness with the ambient humidity, so the increase of the inter-needle sliding, is quite instantaneous. Therefore it cannot account for the very slow strain encountered in the creep of wet gypsum plaster. We have proposed recently that this phenomenon finds its origin in a phenomenon called reaction-driven pressure solution creep. When a sample is submitted to an external load, local stresses appear at the needle contacts. These stresses increase the solubility of gypsum, which accordingly dissolves in the liquid films. The dissolved gypsum then diffuses, and precipitates when arriving in non-stressed regions, where it recovers its initial solubility. This transfer of matter leads to a macroscopic plastic strain of the sample. The thicker the liquid slab, the faster the matter transfer, the larger the creep strain. The phenomenon is said reaction-driven, because the chemical reactions (dissolution and precipitation) are the slowest steps, and then control the kinetics of the creep. Therefore when calcium-complexing chemicals adsorb at the crystals surface, thus hindering these heterogeneous reactions, creep has been seen to be slowed down (Pachon-Rodriguez et al., 2011).

In order to find the best potential anti-creep products, we measure here the dissolution kinetics of gypsum in various aqueous solutions of phosphonates, both simple molecules and polymers, well known for their calcium-chelating action. This scan of numerous phosphonates leads to the identification of the best dissolution inhibitors. The actual anti-creep effect of these phosphonates is tested in a humidity-controlled rheometer on gypsum plaster samples manufactured with these phosphonates. In addition to these parameters also the texture of the poly-crystalline assemblage, as determined by crystal habit and dimensions, has been found to play a role in the macroscopic mechanical behavior of gypsum-based materials.

MATERIALS

The investigated additives are the following phosphonates:

- HEDP (hydroxyethylidene – 1.1 diphosphonic acid), sodium salt at pH 11.5
- ATMP (Aminotrimethylenephosphonic acid), sodium salt at pH 10.5
- EDTMP (Ethylenediaminetetramethylenephosphonic acid), sodium salt at pH 7.0
- DTPMP (Diethylenetriaminepentamethylenephosphonic acid), sodium salt at pH 7.0
- HMDTMP (Hexamethylenediaminetetramethylenephosphonic acid), potassium salt at pH 7.0
- Four different poly-aminophosphonates with alkylene oxide functional groups of increasing molecular weight – from 2 ethylene oxide groups per molecule to 45 alkylene oxide groups per molecule, named P1, P2, P3 and P4. All of them neutralized as sodium salts at pH 7.0.

The plaster used is an industrial plaster from a plasterboard production plant, with high purity hemihydrate and minor components of dihydrate and soluble anhydrite.

HOLOINTERFEROMETRIC EXPERIMENTS

To measure the dissolution rate constant, representative of the reaction kinetics of gypsum in contact with the additive aqueous solution, we have made use of digital holographic interferometry, a non-conventional optical technique. This device is often used in solid mechanics for study vibrations and in fluid mechanics to study flows. We have adapted the method in order to access in real time to the bidimensional concentration field in an aqueous solution above a dissolving gypsum single crystal (Colombani and Bert, 2007).

During an experiment, a digital hologram, i.e., a tridimensional phase picture, of a 10x10x40 mm³ transparent cell containing the aqueous solution is first recorded, constituting the so-called reference hologram. Subsequently a 6x6x0.5 mm³ sample of a cleaved gypsum single crystal from Mazan quarry (France) is placed at the bottom of the cell. Digital holograms are then recorded during the dissolution of the crystal in the liquid (typically during one day). The interference between these holograms and the reference hologram are carried out numerically and brings the phase difference in

the liquid between time t and the reference time, from which the concentration evolution in the cell with time is deduced. The fit of the concentration curves in the liquid with their theoretical expression, brings the dissolution rate constant of the mineral in the aqueous solution. The first advantage of this technique is that it is carried out in a quiet liquid, no flow blurring the dissolution rate as in standard solution chemistry dissolution experiments. So the measured coefficient is a pure surface reaction rate constant. Its second main advantage is that it enables to observe the interface where the dissolution proceeds, instead of computing the dissolution rate from concentration measurements far from the surface.

The dissolution rate constants from all the investigated admixtures are collected in Table 1. It can be immediately seen in these results, from the lower value of the rate constant in presence of phosphonate, that all the chemicals influence the gypsum-solution reaction in slowing down the transfer from solid to liquid. All measurements have been performed with a concentration of product of 1%. It should be noted that for two products, precipitates appeared during the experiment, making the rate constant measurement impossible.

Table 1. Dissolution rate constant of the various phosphonates.

Product	Dissolution rate constant (mol m ⁻² s ⁻¹)
set plaster as it is	$4.6 \cdot 10^{-5}$
P1	$4.5 \cdot 10^{-6}$
P2	$1.6 \cdot 10^{-5}$
P3	$8.9 \cdot 10^{-6}$
P4	$8.3 \cdot 10^{-6}$
EDTMP	$4.9 \cdot 10^{-6}$
ATMP	$7.1 \cdot 10^{-6}$
DTPMP	precipitation observed
HEDP	precipitation observed

HUMID CREEP EXPERIMENTS

The measurements have been performed with a rotational rheometer (Physica MCR 301), with a plate-plate measuring system. The plates used are serrated (rough surface) plates of 25 mm diameter. The gap has been set for all the experiments to 3 mm, the sample thus being a disk 25 mm in diameter and 3 mm in height. The plaster has been mixed with water in a water-to-plaster ratio of 0.7 by weight. The phosphonates have been added at two different dosages: 0.1% and 0.3% active phosphonic acid over plaster weight. The plaster slurry has been mixed in a mechanical stirrer with turbine blade for 1 minute at 1200 rpm and loaded in the measuring system while still plastic. The measurements have started 3 minutes after the first contact of plaster and water. The measuring system is contained in a chamber saturated with water vapor (humidity measured at 92% to 95%). The plaster has been allowed to set in the measuring system. After the setting it has been allowed a resting/curing time of 30 minutes to completely develop the microstructure of gypsum, before starting the creep experiment. The sample has been subject at a shear

stress of 10 kPa while being subject to an axial compression of 10 kPa for a duration of 2h25. Subsequently the shear stress has been removed and the relaxation of the sample has been recorded.

Setting time. The setting of plaster is followed through its volume changes. All the phosphonates cause an increase in setting time, which is larger the higher the dosage. The variation of setting time shows almost the same trend with the molal concentration of the phosphonate in solution for all the products, except for HEDP and DTPMP which show a smaller increase on increasing dosage, as reported in Figure 1. These products, HEDP and DTPMP, are the ones for which a precipitation is observed in the experiments of holographic interferometry, and we may suggest that it is the Ca salt of the phosphonate which is precipitating, thus reducing its effect at the highest concentration.

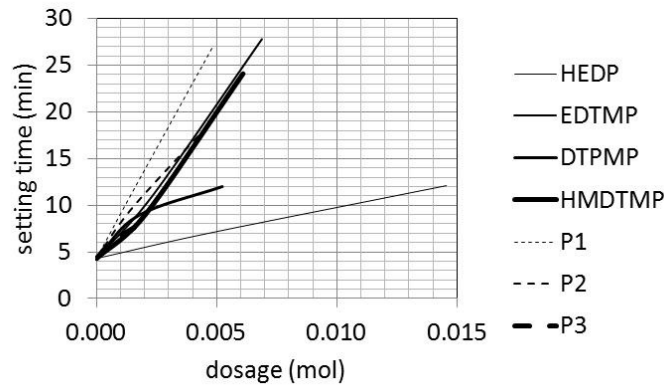


Figure 1. Setting time as a function of concentration.

Creep. The creep and relaxation of gypsum without admixtures is shown in Figure 2 (a). The deformation has an important elastic contribution, which is recovered upon removal of the stress. A visco-elastic deformation is also present which is slowly recovered upon unloading of the sample. Finally there is an irreversible plastic deformation, and the strain rate measured on the final linear portion of the curve is $2,165 \cdot 10^{-9} \text{ s}^{-1}$. The compliance of the sample is $J = 7.70 \cdot 10^{-8} \text{ Pa}^{-1}$, a value which corresponds to the complex modulus G^* measured in a frequency sweep within the linear domain, as shown in Figure 2 (b). The measurement has been performed at an imposed stress of 10 kPa resulting in a strain of $2.7 \cdot 10^{-4}$. The complex compliance $J^*(\omega)$, reciprocal of the complex modulus $J^*(\omega) = 1/G^*(\omega)$, is related to the creep compliance by Fourier transform, and the correspondence between the two indicates that the measurement is not affected by instrumental artifacts.

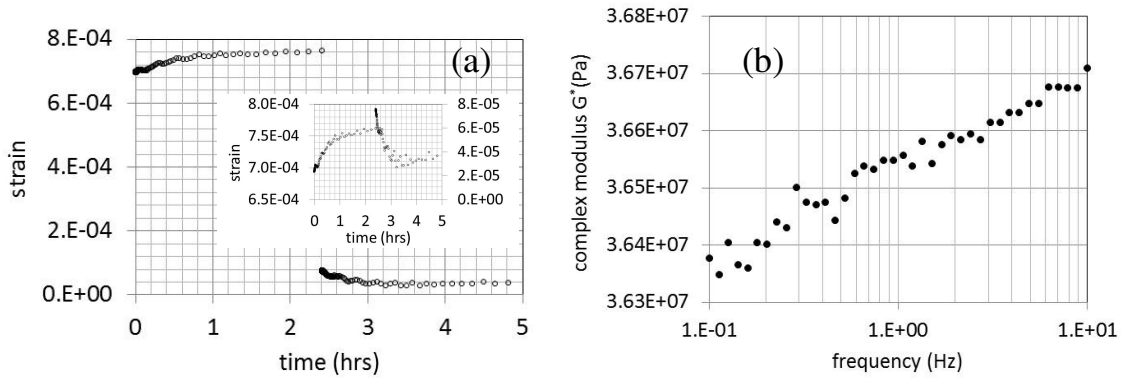


Figure 2. Creep and relaxation for the set plaster without admixtures. In the inset the curves are shown on two different scales (a). Complex modulus as a function of frequency (b).

The qualitative creep behavior of set plaster with the phosphonate admixtures is similar, with differences in the instantaneous elastic deformation and in the long term plastic creep rate. In Figure 3 (a) and (b) are reported the creep curves for the small molecule phosphonates at dosage 0.1% and 0.3% respectively.

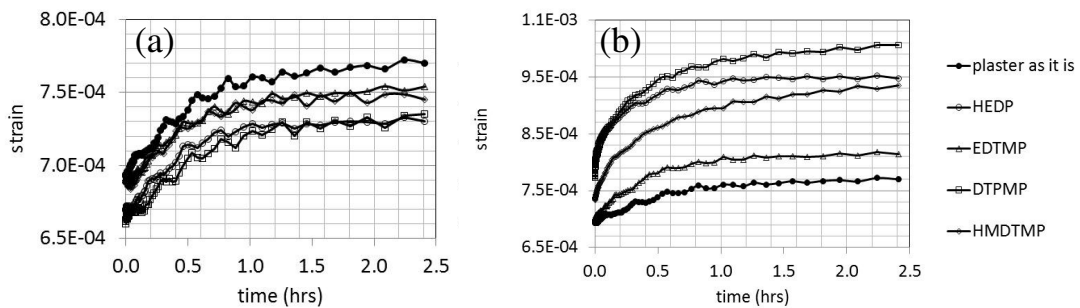


Figure 3. Creep behavior of set plaster with small molecule phosphonates at dosage 0,1% active matter (a) and 0,3% active matter (b).

The long term plastic creep rate is reported in Table 2. It appears that while at low dosage the compliance is lower in the presence of the phosphonates than in their absence, the opposite is true at higher dosage. Apart from the case of EDTMP the instantaneous elastic deformation is increasing with the admixture dosage. The strain rate is also increasing on increasing dosage, being higher in the presence of phosphonates than for the sole set plaster, again with the exception of EDTMP.

The picture is different in the case of set plaster with the addition of the polymeric phosphonates, as shown in the creep curves reported in Figure 4 and in the plastic strain rates reported in Table 2. In the case of products P1 and P2, at lower dosage the creep behavior is similar to the one of set plaster without admixtures,

while on increasing the dosage the overall compliance reduces and the strain rate gets smaller. The product P3 behaves differently, with performance getting better on increasing the dosage, still being however worse than the plain plaster.

Table 2. Plastic strain rate for set plaster with and without phosphonates.

Product	strain rate (s ⁻¹)	
	set plaster as it is	
	2.165·10 ⁻⁹	
	dosage 0.1%	dosage 0.3%
HEDP	1.048·10 ⁻⁹	3.202·10 ⁻⁹
EDTMP	1.942·10 ⁻⁹	2.096·10 ⁻⁹
DTPMP	1.719·10 ⁻⁹	4.378·10 ⁻⁹
HMDTMP	1.438·10 ⁻⁹	5.252·10 ⁻⁹
P1	1.534·10 ⁻⁹	8.841·10 ⁻¹⁰
P2	1.921·10 ⁻⁹	1.083·10 ⁻⁹
P3	3.363·10 ⁻⁹	2.825·10 ⁻⁹

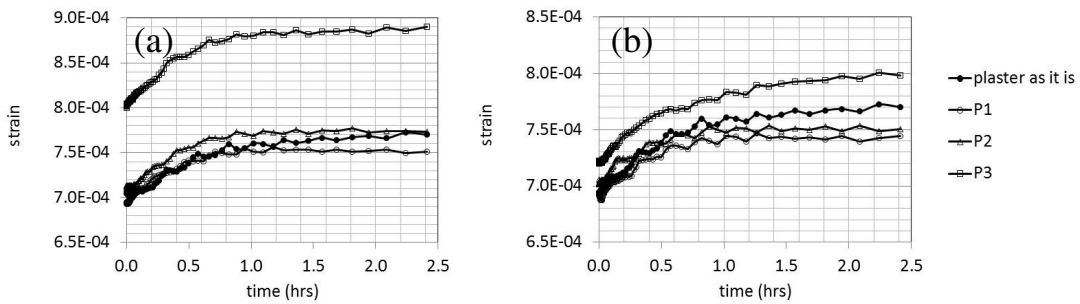


Figure 4. Creep behaviour of set plaster with the polymeric phosphonates at dosage 0,1% active matter (a) and 0,3% active matter (b).

DISCUSSION

The creep behaviour of set plaster in the presence of phosphonates confirms the mechanism of pressure dissolution creep, the phosphonates lowering parallelly the dissolution rate and creep rate. However the overall creep is composed of the sum of an elastic component, a visco-elastic component and a plastic flow. While plastic flow is determined by the pressure dissolution mechanism, the first two components are deeply influenced by the texture of the polycrystalline assemblage, i.e. by the crystal shape and dimensions. Phosphonates are known crystal habit modifiers for calcium dihydrate, and this feature influences the macroscopic results. This may explain that the dissolution rate and strain rate are not strictly correlated, the admixtures acting both on the dissolution and microstructure.

The case appears to be different for small molecule phosphonates and polymeric phosphonates. The first ones precipitate the Ca salt of the phosphonate on increasing concentration in the presence of high Ca contents. This precipitation most probably disturbs the development of the gypsum microstructure during setting at

high dosage, which negatively affects the mechanical behavior of set plaster. Therefore overdosing of these products may affect the set plaster performance, which makes their use quite difficult in practice.

The polymeric phosphonates never precipitate even at high concentration and high Ca loadings and their performance gets better on increasing the dosage. This makes them good candidates as anti-creep admixture. In this case, the best product, easy to use and very effective, is the lowest molecular weight polymer P1, with the highest molal concentration at a given dosage and the best influence of the mechanical behavior.

CONCLUSION

Relying on the assumption that humid creep of gypsum plaster originates in the dissolution of the material, we have measured the dissolution rate constant of various phosphonates, known to adsorb on calcium containing crystal like gypsum. All of them have been seen to slow down the dissolution. Therefore the shear creep of gypsum plasters containing these admixtures has been investigated by humidity-controlled rheometry. All of them but one have been found to lower the creep rate, validating our assumption. Dissolution rate and creep rate are not strictly proportional because the phosphonate influence not only dissolution but also the microstructure of the samples, modifying its mechanical behaviour. Polymeric phosphonates have been found to be better anti-creep candidates, their dosage being less delicate.

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