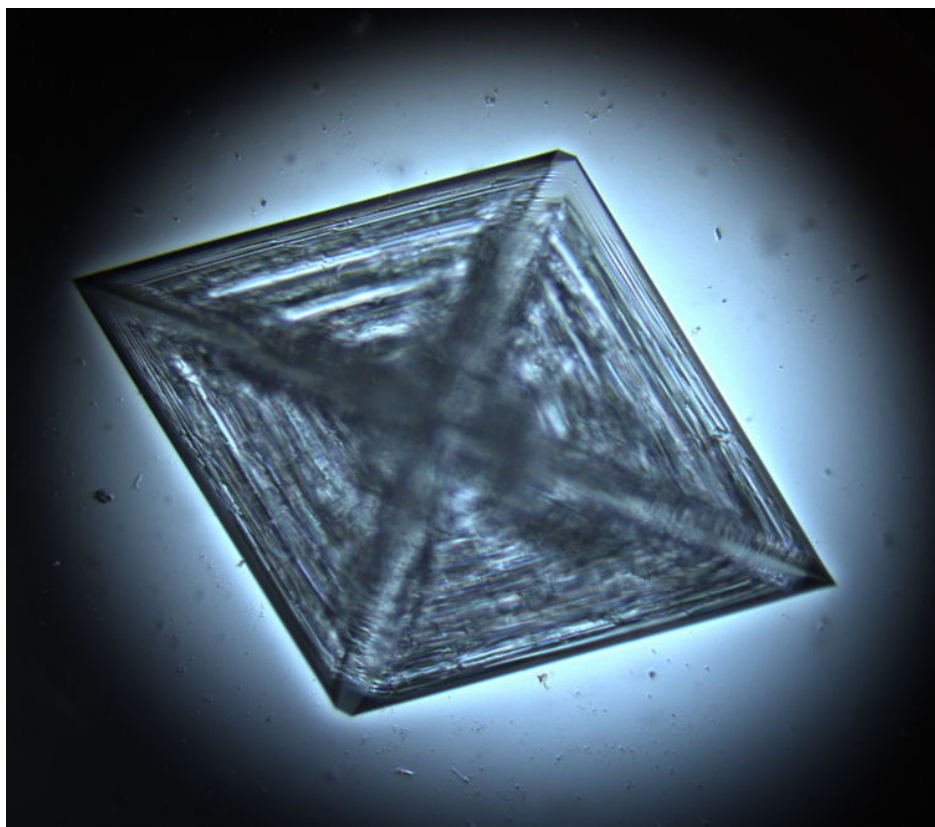


Workshop

CRYSPOM III

Crystallization in porous media



Tróia, Portugal

4-7 September 2012

Workshop Chair

Leo Pel (TU/e) and Teresa Diaz Gonçalves (LNEC)

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Noushine Shahidzadeh-Bonn - UVA (Netherlands)

Rosa M. Espinosa-Marzal - ETH (Switzerland)

Wednesday, September 05, 2012

8 : 3 0 – 8 : 4 5	Opening (Leo Pel / Teresa Diaz Gonçalves)	
8 : 4 5 – 9 : 2 5	<u>Jan Carmeliet</u> , Dominique Derome, Hannelore Derluyn, Robert Guyer, Sergey Churakov	Keynote lecture 1 - Sorption and crystallization induced deformation: from molecular dynamics to macroscopic modeling
9 : 2 5 – 9 : 5 0	<u>Andrea Hamilton</u> and Christopher Hall	Atomic Strain Produced From Mirabilite Crystallisation In Sandstone And Calcium Silicate.
9 : 5 0 – 1 0 : 1 5	<u>Francesco Caruso</u> and Robert J. Flatt	A “new” Correns’ experiment
1 0 : 1 5 – 1 0 : 4 0	Julie Desarnaud and <u>Noushine Shahidzadeh-Bonn</u>	Study of the kinetics of salt crystallization during rewetting/drying and humidity cycling
1 0 : 4 0 – 1 1 : 1 0	Coffee break	
1 1 : 1 0 – 1 1 : 5 0	<u>George W. Scherer</u> ¹ and Rosa M. Espinosa-Marzal ^{1,2}	Keynote lecture 2 - Kinetics of crystallization in pores
1 1 : 5 0 – 1 2 : 1 5	Hannelore Derluyn, <u>Dominique Derome</u> , Iwan Jerjen, Jan Dewanckele, Veerle Cnudde, Eberhard Lehmann and Jan Carmeliet	Characterizing salt transport and crystallization damage in porous limestone with neutron radiography and X-ray micro-tomography
1 2 : 1 5 – 1 2 : 4 0	Hannelore Derluyn, Peter Moonen and Jan Carmeliet	Numerical modeling of crystallization induced damage processes
1 2 : 4 0 – 1 3 : 0 5	<u>Eduardo E. Alonso</u> and Anna Ramon	Gypsum crystal growth under bridge foundations
1 3 : 0 5 – 1 4 : 0 5	Lunch	
1 4 : 0 5 – 1 4 : 4 5	<u>Marc Prat</u>	Keynote lecture 3 - How to make crusty or patchy efflorescence
1 4 : 4 5 – 1 5 : 1 0	<u>Sonia Gupta</u> , Henk Huinink and Leo Pel	Effect of ferrocyanide ions on the drying behavior of NaCl contaminated porous material
1 5 : 1 0 – 1 5 : 3 5	<u>Barbara Lubelli</u> , Timo G. Nijland and Rob P.J. van Hees	Effect of inhibitors on sodium sulfate crystallization
1 5 : 3 5 – 1 6 : 0 0	<u>J.M.P.Q. Delgado</u> , A.S. Guimarães and V.P. de Freitas	Salt Transport in Porous Media: Preliminary Experimental and Theoretical Analysis of Salt Diffusion
1 6 : 0 0 – 1 6 : 3 0	Coffee break	
1 6 : 3 0 – 1 6 : 5 5	<u>J. Dewanckele</u> , W. de Boever, T. de Kock, M.A. Boone, M.N. Boone, L. Brabant, G. Fronteau, L. Van Hoorebeke, V. Cnudde and P. Jacobs	Influence of limestone microstructure on gypsum crystallization
1 6 : 5 5 – 1 7 : 2 0	<u>Vânia Brito</u> , Teresa Diaz Gonçalves	Effects of NaCl and NaNO ₃ on the capillary suction, drying kinetics and vapour permeability of three building stones

17 : 20 - 18 : 20	<p>Poster Session:</p> <ul style="list-style-type: none"> • <u>J.M.P.Q. Delgado</u>, A.S. Guimarães and V.P. de Freitas - Salt Degradation in Stone of Historical Buildings: The Importance of Water Absorption Coefficient • Jorge Feijoo Conde¹, Teresa Rivas Brea¹, Nóvoa X.R.², <u>Iván de Rosario Amado</u>¹ and Javier Taboada¹ - Extraction of sulphates by electromigration in two different granites • <u>Jacek Chwast</u> and Jan Elsen - Gypsum efflorescence on clay brick masonry • <u>Nadine Lindström</u>, Nicole Heitmann, Kirsten Linnow and Michael Steiger - Crystallization behavior of NaNO₃-Na₂SO₄ salt mixtures in sandstone and comparison to single salt behavior • <u>Paulina Faria</u>, Vitor Silva - Capillary and drying of natural hydraulic lime and of air lime based mortars • Maria Idália Gomes, <u>Teresa Diaz Gonçalves</u>, Paulina Faria - Capillary water absorption of unstabilized and stabilized earth materials: anomalous time scaling behavior • <u>S.Gupta</u>, L.Pel, Michael Steiger - Influence of ferrocyanide ions on NaCl crystallization in the mixture of salts
19 : 30	Porto wine at the penthouse (sunset is at 20:00)
20 : 30	Dinner

KEYNOTE LECTURE

Sorption and crystallisation induced deformation: from molecular dynamics to macroscopic modeling

Jan Carmeliet^{1,2}, Dominique Derome², Hannelore Derluyn², Robert Guyer³, Sergey Churakov⁴

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³LANL/University of Nevada, USA

⁴Paul Scherrer Institute, Switzerland

ABSTRACT

Adsorption originates at the molecular scale from the interactions between the atoms of the solid skeleton and the molecules of the fluid. When the size of the pores is in the order of the range of the molecular interactions (micro or nanoporous materials), a mechanical pressure arises orthogonal to the porous interface leading to sorption induced deformations (swelling). To study sorption induced deformations in microporous materials, a poromechanical approach is used taking into account explicitly solid-fluid interactions arising in complex random microporous materials. To determine the mechanical effects of adsorption, the amount of adsorbed fluid in the medium has to be known in function of both the chemical potential of the fluid and the volumetric strain of the porous medium. This information can be gained by experiments and modeling.

In this presentation, we present different approaches to determine the macroscopic material properties including coupling coefficients: molecular dynamics, coarse grain simulation and the dependent domain approach to link different scales in hierarchical materials. In the dependent domain theory, the global material behavior results from the interaction of basic elements situated at different scales and characterized by statistical distributions. Upscaling is taking into account for hierarchical materials, showing geometric disorder and anisotropic behavior at lower scales. Towards developing a framework for the determination of sorption induced deformations using dependent domain theory and computational upscaling, which allows to determine nonlinear coupling coefficient and the hysteretic coupled behavior, we observe experimentally by high resolution X-ray tomography different microstructures containing microporous materials. In particular, we study hierarchical materials like wood, which can be used to develop our understanding of shape memory effects upon moistening.

Finally we will extend the approach towards chemical induced deformations. In particular we discuss as an example the state and dynamics of water and cations in pure and mixed Na-Cs-montmorillonite as a function of the interlayer water content using Monte Carlo and classical, molecular-dynamics methods.

Atomic strain produced from mirabilite crystallisation in sandstone and calcium silicate

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ABSTRACT

We show the evolution of atomic level strain from mirabilite crystallisation in Berea sandstone and calcium silicate plate during cooling. Using white beam synchrotron X-ray diffraction we can measure face specific displacements in lattice d-spacing and show how mirabilite compression varies according to crystallographic face being compressed. We present for the first time, a view of in pore crystallisation that sees the crystal as a faceted object. We compare this to hydrostatic compression of mirabilite in a diamond anvil cell and show that in this environment, mirabilite loses crystallinity at room temperature and ~5.7 kbar of pressure. We examine different pore environments provided by sandstone compared to the loosely packed xonotlite needles in calcium silicate board. We also show how quartz, kaolinite and xonotlite d spacings vary with temperature and crystallisation pressure from mirabilite.

A “new” Correns’ experiment

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ABSTRACT

The growth of salt crystals within the porous network of stones is the single most important cause for their decay [1,2,3]. Such growth can cause stresses sufficient to overcome the tensile strength of a stone and turn it into a powder. These stresses are directly related to the crystallization pressure. Therefore, a quantitative estimation and modeling appear to be necessary for a thorough understanding of the damage by salt crystallization.

Correns and Steinborn performed an early experiment for the determination of crystallization pressure [4,5,6]. Thanks to an ingenious optical system, they measured the vertical displacement of a loaded aluminum rod (whose end was covered with a glass socket) pushing on a potassium alum monocrystal ($\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$) in its supersaturated solutions. Then, they related such a displacement to the crystallization pressure as a function of the supersaturation ratio of the solutions. Interestingly, they obtained an incomplete equation of the crystallization pressure in good agreement with their experimental data.

The scope of this work is a study of the original experiment, recognizing and avoiding possible experimental artifacts that Correns and Steinborn probably neglected [6]. Up to now, we have considered supersaturated potassium alum solutions from $c/c_s = 1.0$ to $c/c_s = 1.5$, verified their stability to nucleation and measured their pH (in an attempt to know more about aluminum speciation). Although the chemistry of aluminum at low pH values is complex [7], such stability is the main reason for continuing to work with potassium alum (probably used at Correns’ times for its ability to produce very good monocrystals). Also, we have characterized by optical profilometry the (111) surface of five commercial potassium alum crystals with 0.1° and 1° orientation accuracies. We are now working on the design and production of a stainless steel glass covered pushrod to be connected to a load cell of a universal testing machine. This will eventually be used for carrying out the crystallization pressure measurements.

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Study of the kinetics of salt crystallization during rewetting/drying and humidity cycling

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ABSTRACT

In this paper, we reveal the major role the recrystallization dynamics plays in the way different salts can cause damage to stone under different environmental conditions. There are two ways in which a salt, once crystallized, can take up water again: by bringing it in contact with liquid water (dissolution) or with water vapour (deliquescence). We compare the kinetics of salt recrystallization for different salts (NaCl, KCl, Na₂SO₄), after either deliquescence or dissolution followed by drying, for several cycles.

We find that deliquescence/recrystallization with humidity cycling leads to the growth of salt crystals by expulsing impurities. For salts such as NaCl that have only one crystalline form, this leads to the growth of less nuclei which can achieve larger size. In this process, the solution can reach high concentration before the crystal growth. The consequence of the latter is the faster growth of a smaller number of crystals with the progression of cycles. These results can be a plausible explanation for why subsequent humidity cycling with NaCl leads to an irreversible dilation and the gradual expansion of the material.

For Na₂SO₄ which has different crystalline forms (hydrated and anhydrous), the fact that high salt concentrations are reached after deliquescence followed by drying, favors the direct precipitation of anhydrous Na₂SO₄. The results show that the crystallization of the anhydrous salt generates only very small stresses that hardly damage the stone. On the contrary, with rewetting/drying sodium sulfate can lead to severe damage because the thenardite microcrystals dissolve very rapidly, and remaining crystals act as seeds to form large amount of hydrated crystals creating grape-like structures that expand rapidly. These clusters generate stresses larger than tensile strength of the stone. These results shed some light on how the kinetic pathway of crystallization plays a role on the way the same salt can cause damage in some conditions and not in others.

KEYNOTE LECTURE

Kinetics of crystallization in pores

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ABSTRACT

The conventional Johnson-Mehl-Avrami-Kolmogorov (JMAK) does not correctly describe the growth of crystals in a porous network, because it does not take account of confinement. However, there are extensions of that model that do describe growth confined within pores that are cylindrical, spherical, planar, or polyhedral, and where nucleation occurs on the pore walls and/or in the solution [1,2]. In this paper, we extend these models to describe growth in a network of pores, and compare their performance in describing experiments on growth of sodium sulfate salts in the pores of limestone upon cooling. The analysis takes account of the changing supersaturation in the pores, and the resulting time dependence of the crystal growth rate. The implications of these models for the poromechanical prediction of crystallization pressure are developed, and used to interpret measurements of the dilatation of limestone that results from growth of salt.

First we consider the model obtained by Villa and Rios [Error! Bookmark not defined.] for growth at rate $G[t]$ from a fixed number of sites per unit area, N_S , confined within a cylinder of radius R . Use of this model implies that the stone can be represented as a network of cylindrical pores joined at nodes, as in Figure 1, and that the salt nucleated in one pore cannot branch into other pores in the network.

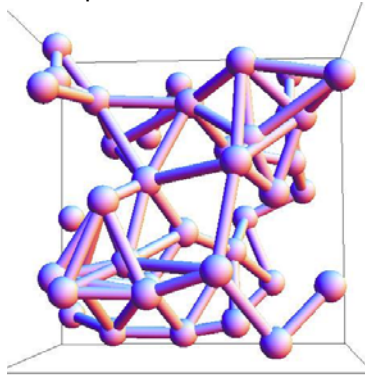


Figure 1: Schematic of pore network in stone

If the nucleation rate is high enough so that there is at least one nucleus between every pair of nodes in the pore network, then this model is ideal. If the nucleation rate is low, then by the time that a significant amount of crystallization has occurred, the length of each crystal is much larger than the pore diameter, so growth is primarily parallel to the axis of the cylindrical pore. In that limit, the volume fraction of crystals is

$$V_C[\theta] \approx 1 - \exp[-4\pi\lambda\theta] \quad , \quad \theta > 2, \quad \lambda \leq 0.003 \quad (1)$$

where $\lambda = R^2 N_S$ and the reduced time is

$$\theta = \int_0^t \left(\frac{G[t']}{R} \right) dt' = \int_0^t \left(\frac{K(\beta[t'] - 1)}{R} \right) dt' \quad (2)$$

where β is the thermodynamic supersaturation and K a kinetic parameter. Growth stops when the concentration is reduced to the solubility limit ($\beta = 1$). Unless diffusion from neighboring pores is allowed, no pore will be completely filled with salt, so little or no crystallization pressure will be produced. When such diffusion is allowed, this model provides a good fit to data for crystallization of sodium heptahydrate and mirabilite in limestone, and it predicts that a residual supersaturation will exist that will contribute to crystallization pressure.

A different model is required, if the salt is able to branch into the other pores at intersections in the network [1]. In that case, filling of pores with crystals requires diffusion to occur over a distance comparable to the radius of the crystallized region, so the kinetics are entirely different, and high crystallization pressure is less likely.

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Characterizing salt transport and crystallization damage in porous limestone with neutron radiography and X-ray micro-tomography

Hannelore Derluyn^{1,2}, Dominique Derome², Iwan Jerjen², Jan Dewanckele³, Veerle Cnudde³, Eberhard Lehmann⁴, Jan Carmeliet^{1,2}

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ABSTRACT

Information on saline transport, pore filling and fracturing due to salt crystallization is essential for the understanding of the coupling between transport and mechanical processes related to salt weathering. This knowledge is required for the selection of the best suited materials and conservation methods for civil constructions and our cultural heritage. Additionally, such datasets are needed to advance numerical modeling of crystallization in porous media.

Our aim is to collect threefold information on liquid transport, salt distributions and fracturing processes on the same sample. Savonnières limestone is chosen as the porous material for our study and samples are subjected to repeated wetting-drying cycles. A hydrophobic treatment is applied on the top side and vapour and liquid tight foil is applied on the lateral sides. The hydrophobic treatment is intended to prevent salt efflorescence at the surface and to induce in-pore crystallization. Repeated uptake and drying of a salt solution should lead to the accumulation of an amount of salt inside the material sufficient for (1) the quantification of salt distributions and (2) for inducing fracturing. Due to the repetitive character of the experiments, non-destructive techniques are needed. As hydrogen highly attenuates neutron radiation, transmission-based neutron imaging is a well suited technique to study liquid transport. The higher spatial resolution achievable with X-ray micro-computed tomography (μ CT) allows assessing porosity changes and fracture formation due to salt crystallization. Therefore we opted to combine neutron radiography and X-ray μ CT on our samples. Additionally, the adequacy of these two techniques for the study of salt crystallization in porous materials is presented.

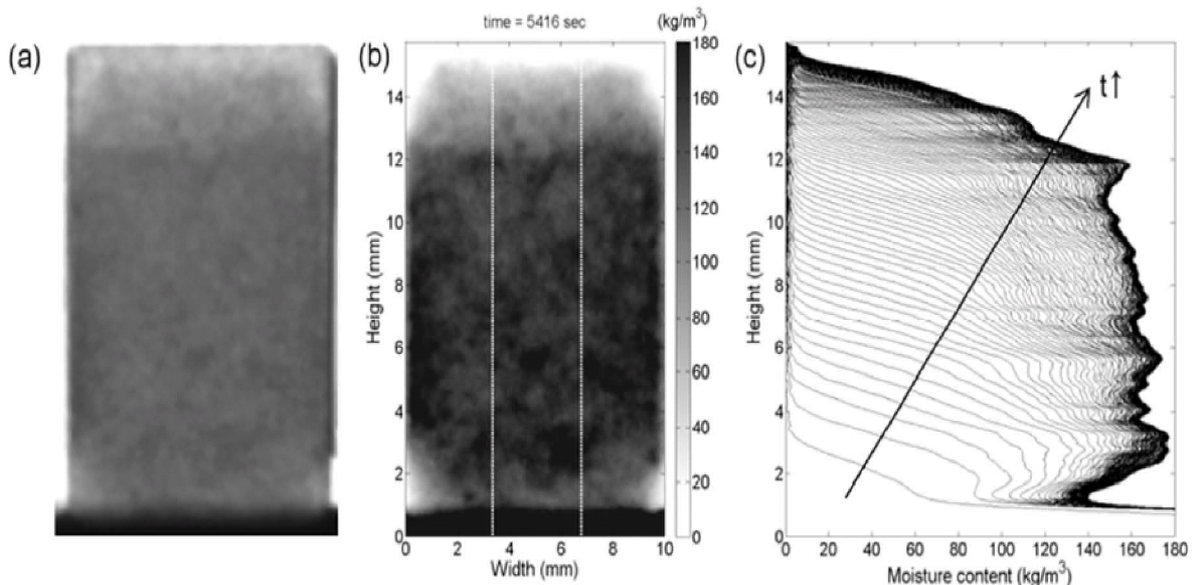


Figure 1: (a) Transmission image and (b) moisture distribution of a Savonnières sample, hydrophobically treated on the top side, after capillary uptake of water. The white lines border the central area over which we average to obtain the moisture profiles. (c) The moisture profiles at 32 s intervals.

We will present the results of two experimental test series conducted on samples of Savonnières limestone. This limestone has 5 pore systems with characteristic sizes ranging between 100 nm and 1 00

pm. The porous structure is depicted in Fig. 2a. All samples were scanned in their initial state in a laboratory X-ray μ CT setup. In the first test series, capillary uptake (at about 25°C) of water, 5.8 molal sodium chloride solution and 1.4 molal sodium sulfate solution was visualized with neutron radiography on prismatic samples of 10x10~15 mm³. Moisture profiles are derived from the 2D moisture distributions (see Fig. 1) and are further analyzed determining the moisture penetration coefficient and the moisture diffusivity. An important decrease of these two coefficients is observed for the salt solutions compared to water uptake. This decrease can be attributed to the change in surface tension σ and viscosity η . The penetration coefficient scales as $\sqrt{\sigma/\eta}$ and the diffusivity as σ/η . This indicates that the calcitic Savonnieres stone matrix does not read with the water or salt solution.

In the second test series, drying (at 45°C) was visualized with neutron radiography on prismatic samples of 10x10x8 mm³. Smaller samples were taken with the aim of characterizing the first and the start of the second drying period during a time span of about 10 hours. Pore blocking by sodium sulfate crystals is observed leading to a slower drying with every subsequent wetting-drying cycle.

Moreover, sodium chloride precipitates, deformation and damage are observed already after the first wetting-drying cycle. Consecutive wetting-drying cycles cause additional deformation and damage. Samples containing precipitated sodium sulfate salt get damaged by the rewetting step, but only when sufficient salt is present in the porous structure, i.e. after several wetting-drying cycles.

Salt profiles are quantified based on neutron and X-ray image analysis of the dried samples. The zone of salt precipitation is located at the upper part of the samples, partly in the hydrophobized zone and partly just below this zone. This is caused by the long first drying period of Savonnieres limestone. The Porosity reduction due to salt precipitation was quantified up to the resolution of the laboratory X-ray pCT datasets (14 μ m). These datasets also revealed the damaging character of the salts as the fracture morphology could clearly be identified (see Fig. 2c). The tomographic study was further extended by acquiring synchrotron radiation X-ray tomographic datasets of cylindrical Savonnieres samples (3.3 mm diameter, resolution of 3.7 μ m). The salt distribution before and after drying was visualized and quantified for repeated wetting-drying cycles (see Fig. 2b). This let us conclude that salt crystals precipitate in all pore systems of Savonnieres limestone. The damage most likely occurs in the mechanically weak zones (zones with less cohesion between the calcite grains), as these zones are accessible to saline liquids.

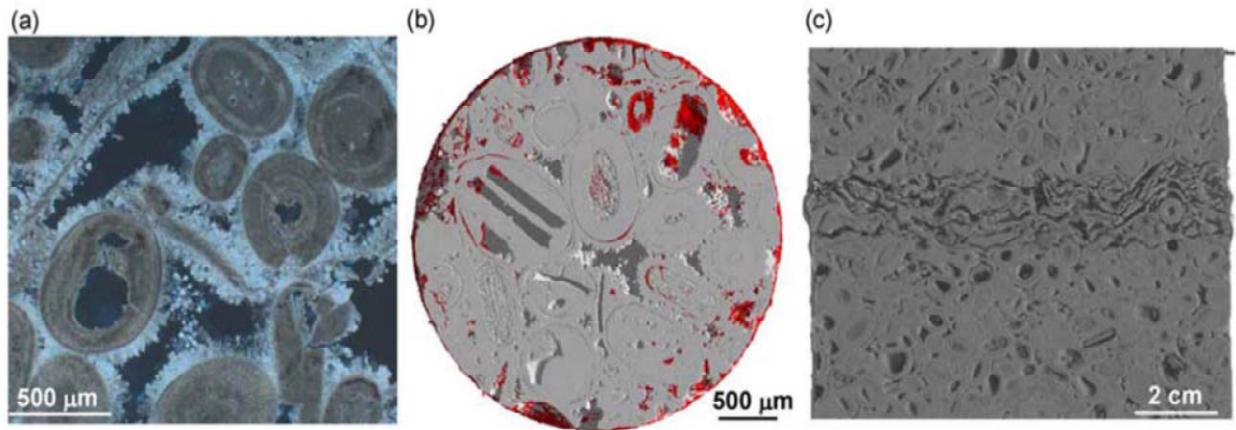


Figure 2: (a) Thin section of Savonnieres limestone visualized by optical microscopy. (b) Cross-sectional slice obtained from a 3D synchrotron radiation X-ray μ CT dataset of a dry Savonnieres sample, with precipitated NaCl crystals in red. (c) Vertical slice of upper part of a dry sample after repeated wetting-drying cycles within 1.4 molal sodium sulfate solution, as obtained from a 3D laboratory X-ray μ CT dataset.

Numerical modeling of crystallization induced damage processes

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ABSTRACT

Water and dissolved salt ions penetrate into building materials due to diffusive and convective transport. Upon changes in the environmental conditions (temperature and vapour pressure), salt can crystallize at the surface (efflorescence) or inside the material (subflorescence). Subflorescence is accompanied with the development of crystallisation pressures in the porous material, which may lead to spalling and cracking of the solid material matrix. To this day, the mechanism of crystallisation in confined conditions and the related damage processes, as well as the computational modelling, are subject of scientific debate.

This presentation follows another talk at Crispom III [1]. In [1] we discussed the use of neutron radiography and X-ray micro-tomography for the visualization and quantification of saline transport, salt distributions and fracture morphology in Savonnières limestone. We found that damage due to crystallization most likely occurs in mechanically weak zones of the material, which are accessible by liquids. Based on the experimental results, constitutive relations can be formulated and implemented in a finite element model combining: (1) a coupled heat, moisture and salt transport model; (2) a crystallization model and (3) a model describing the mechanical coupling between salt, moisture and the solid matrix. The coupling of the transport and crystallization model has been described in [2] and was presented during Crispom II [3]. In this presentation we will focus on the coupling with the mechanical behaviour using the theory of poromechanics [4]. The fracturing due to salt crystallization pressures is incorporated using a strong discontinuity framework as described by [5]. The properties to describe ion transport, crystal growth and crystallization pressures for two single salts, sodium sulfate (Na_2SO_4) and sodium chloride (NaCl), have been included. All properties are both temperature and concentration dependent. Sodium sulfate has different crystal phases that form upon cooling or drying: mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) and thenardite (Na_2SO_4). Sodium chloride has one stable crystal phase above the freezing point: halite (NaCl). Various climatic conditions can be imposed and the response of a structure can be assessed for longer time periods (decades), as also described in [6].

In this presentation the model performance will be validated by repeating the wetting-drying experiments discussed in [1] by numerical simulations. The applicability of the model for cooling induced damage or damage induced by deliquescence cycles will be illustrated as well. We will show how, by varying model parameters, numerical modeling can help in understanding damage due to salt crystallization and how modeling studies can complement experimental results

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Gypsum crystal growth under bridge foundations

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ABSTRACT

Gypsum crystal growth in a deep stratum located below the massive Pont de Candí pile foundations explains the important heave experienced by the central pillars after construction [1]. The 413 long bridge is located in the high speed Madrid-Barcelona railway. Pillars are founded on groups of 3x3 deep bored piles 1.65 m in diameter with an average length of 20 m. Piles are socketed in a stiff Eocene claystone having a significant content of gypsum and anhydrite. The geologic formation has been studied in detail [2] due to the severe swelling experienced by the nearby Lilla tunnel floor.

A heave rate ranging from 5 to 10 mm/month was measured by levelling the bridge structure. Vertical displacements were also measured at ground surface in an area 200 meters wide along the bridge axis. Contours of equal vertical displacements were drawn. They had an elliptical shape whose major axes were parallel to the direction of water flow. Deep continuous extensometers were installed inside boreholes. Swelling strains were recorded at deep positions, below piles' tip (Fig. 1). An active layer, 12-15 m thick, was defined. Time records of vertical displacements exhibited a constant heave rate with no indication of slowing down in the relatively long recording period (2.5 years).

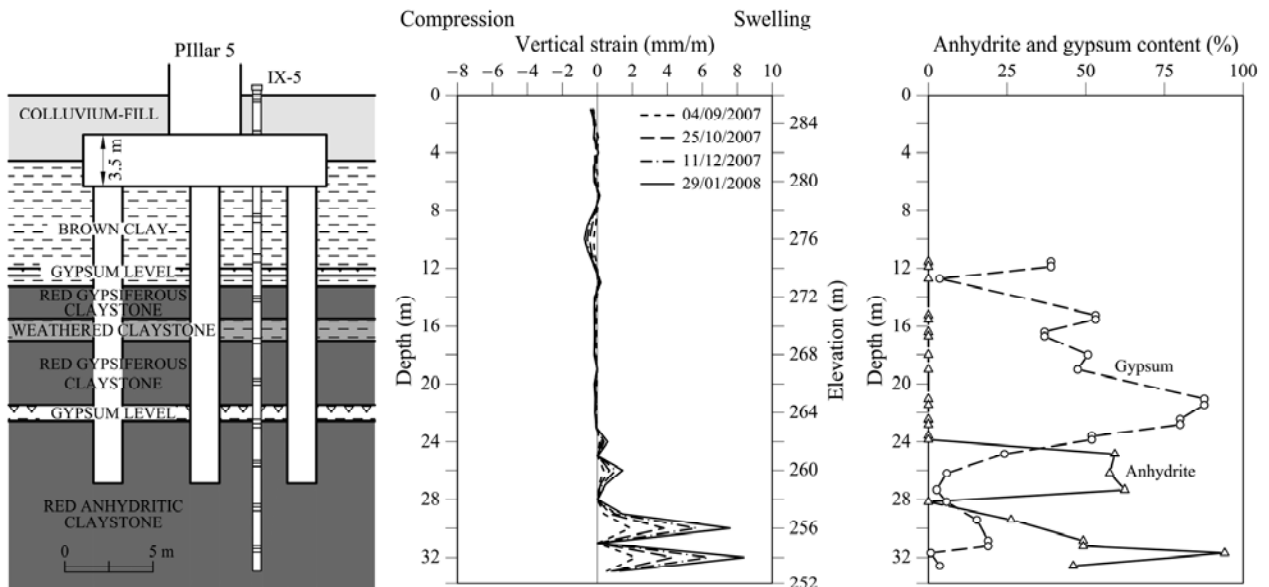


Figure 1: Measurements in extensometer IX-5 (Initial reading: 12/July/2007) and profiles of anhydrite and gypsum content (X-ray diffraction technique)

Figure 1 shows a typical variation of gypsum and anhydrite content with depth. The comparison between the vertical strains and the distribution of anhydrite and gypsum shows that swelling strains were associated with the presence of anhydrite. Gypsum crystals were observed in cores recovered from boreholes at depths corresponding to the active layer. Needles of gypsum crystals, oriented perpendicular to the plane of discontinuities, filled partially open discontinuities. Some of the crystals seemed to be very recent. The open discontinuities partially clogged with gypsum needles allow the flow of water within the active zone. Flake gypsum crystals growth inside the clay matrix was also observed. Since the calcium sulphate concentration of water in equilibrium with anhydrite is higher than the saturation concentration with respect to gypsum, at the temperatures present in Pont de Candí rock mass (Fig. 2), anhydrite will tend to dissolve and gypsum will precipitate.

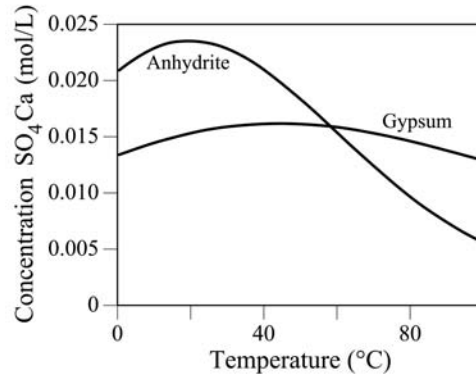


Figure 3: Equilibrium concentration of SO_4Ca water with respect to gypsum and anhydrite

A campaign of hydraulic cross-hole tests revealed a system of hydraulically connected horizontal discontinuities in the active expanding layer. Low values of permeability were found above and below the active zone. The crystallization of gypsum in discontinuities produces a flat-jack effect pushing upwards the soil and rock layers above the active zone, as well as the bridge pillars. It is believed that the set of boreholes and foundation piles performed connected the upper aquifer with the deeper fissured anhydritic claystone, triggering the heave phenomenon.

A model for gypsum crystal growth has been formulated within a general framework for hydro-mechanical analysis for saturated porous media [3]. The dissolution of anhydrite and precipitation of gypsum has been taken into account in the formulations [4]. The model also keeps track of solute evolution. Kinetic equations, adapted from [5], describe the rate of mass precipitated or dissolved in terms of the current concentration of the solute and the concentration for saturated conditions. The precipitation or dissolution of crystals will reduce or increase porosity. Strains are calculated from the precipitated crystal volume and the prevailing effective stress.

A column of the foundation material at the position of central pillar was modeled under plain strain conditions [4]. The active layer, 15 m thick, was included between 2 stable layers. A horizontal flow was forced in the active layer. The model is able to reproduce the heave measured at central pillars of the bridge. A sensitivity analysis performed provides an additional insight into the phenomenon.

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KEYNOTE LECTURE

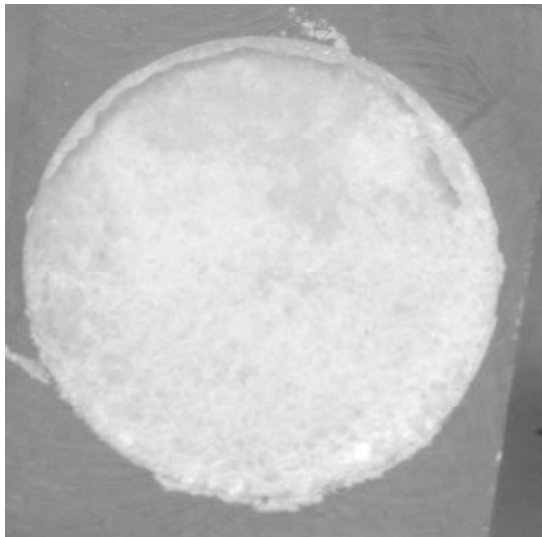
How to make crusty or patchy efflorescence

Prat Marc¹

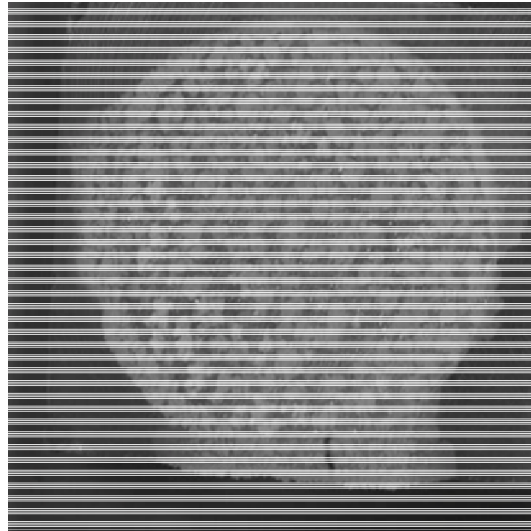
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ABSTRACT

We present an experimental study of drying in the presence of dissolved sodium chloride. The process is characterized by the formation of crystallized salt, referred to as efflorescence, at the evaporative surface of the porous medium. By varying the average size of the beads forming the porous medium, we show that the formation of the crystal layer does not affect significantly the drying process and can even enhance the drying rate when the beads are sufficiently large. By contrast the crystal layer can greatly affect the drying process and even blocks the evaporation process for sufficiently small beads. We therefore show the existence of a transition between the two regimes, namely the blocking regime and the enhanced drying rate regime. It is shown that the two regimes correspond to two different types of efflorescence, referred to as crusty and patchy respectively. Then by varying the initial salt concentration for a given bead size, we show that the interplay between drying and the efflorescence formation leads to a non-monotonous variation of the drying rate with the initial salt concentration when the efflorescence is patchy but not when the efflorescence is crusty.



Crusty efflorescence



Patchy efflorescence

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Effect of ferrocyanide ions on the drying behavior of NaCl contaminated porous material

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ABSTRACT

While the mechanisms of salt damage in porous materials have received considerable attention in recent years, effective treatment methods for ameliorating this problem still remain limited. Recently, the use of ferrocyanide inhibitors has been proposed as a potential preventive treatment method against NaCl damage [1]. However, until now the suitability of these inhibitors for the treatment of salt damage is still under discussion. One of the reasons behind this is lack of adequate experimental data for understanding the moisture and ion transport mechanisms in the porous materials while drying. In lieu of this, a detailed experimental study has been performed to understand the effect of inhibitors on the drying behavior of salinated porous materials at varying environmental conditions. Nuclear Magnetic resonance Technique (NMR) has been used for carrying out non-destructive and quantitative measurements of both the moisture and salt ions content simultaneously. Drying experiments using 3m NaCl solution containing different concentration of potassium hexacyanoferrate (II) trihydrate inhibitor have been performed at varying relative humidity conditions. In a previous study we have reported the drying behavior of salt saturated materials with and without inhibitor at low relative humidity [2]. In this work, further investigation has been done to understand the drying behavior of the bricks at higher relative humidity conditions. We have used fired-clay brick as a model porous material. The relative humidity was varied between 0%, 55% and 70%.

Initially, drying experiments were performed on salt contaminated bricks without inhibitor. The results show that approx. 45% of salt crystallize as efflorescence at high relative humidity (55% and 70% relative humidity) compared to only 6% efflorescence seen at low relative humidity. Also, drying rate of the salt contaminated brick was higher at high relative humidity in comparison to the one dried at low relative humidity. This is due to the formation of efflorescence at high humidity. The salt efflorescence acts as a porous network that increases the effective surface area for evaporation and pumps more and more dissolved salt ions along with the moisture content towards the drying surface seen as efflorescence. Due to transfer of salt outside the material as efflorescence, there was no blockage of pores near the drying surface to hinder evaporation of water (as is the case of bricks dried at low relative humidity) and thus the drying rate increases at high relative humidity. Next drying experiments were performed in the presence of inhibitor. The maximum effectiveness of inhibitor was seen at low relative humidity (0% relative humidity). At low relative humidity in the presence of inhibitor a significant amount of salt crystallize out as efflorescence and a delay in attaining saturation concentration was seen. However, at high relative humidity (55% and 70% relative humidity) not much difference was seen in the amount of efflorescence formed with and without inhibitor. Also, the saturation concentration was attained almost at the same time inside the material.

These results show that the formation of efflorescence changes the drying kinetics of porous materials. The use of ferrocyanide ions as an inhibitor against NaCl damage will be more beneficial in faster drying regions e.g. the regions of low relative humidity and the regions with high air flow rates. For such regions the use of inhibitor helps to crystallize salt outside the materials as efflorescence and can prevent NaCl damage. However, in the regions with high relative humidity the use of inhibitor may not be very beneficial as no significant difference was seen in the drying behavior of the bricks with and without inhibitor.

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Effect of inhibitors on sodium sulfate crystallization

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ABSTRACT

Salt crystallization in porous materials constitutes one of the most frequent causes of decay of buildings in a wide range of environments. Up to now no definitive solution exists to avoid salt crystallization damage, apart from removing either the salt or the moisture. The possibility of making the process of salt crystallization less harmful by means of crystallization inhibitors has only recently been considered. Crystallization inhibitors are ions or molecules able to delay nucleation and to modify the growth rate of the crystals. For some salts, as sodium chloride, the effectiveness of crystallization inhibitors in delaying crystallization and reducing salt crystallization damage under certain well defined conditions has been demonstrated, whereas for other salts, as sodium sulfate, results obtained until are unsatisfactory. In this research a series of systematic investigations on the effectiveness of different types of inhibitor (amino-tris-methylene-phosphonic acid (ATMP) and sodium salt of polyacrylic acid (PA)) for sodium sulfate was carried out. First, the effectiveness of the inhibitors in bulk solution was investigated. Crystallization experiments in bulk solution were performed under different temperature and RH conditions: the weight of the solution was monitored and the occurrence of crystallization checked by optical microscope. Additionally, crystallization experiments in bulk solution were carried out in a XRD chamber with controlled RH (50 and 80% RH) and temperature(20 °C)conditions.

In a second experiment, inhibitors were mixed in during the preparation of a lime-cement mortar. Mortar specimens were made and accelerated crystallization tests were carried out to study the effect of the inhibitors on the development of salt damage.

In this paper the obtained results will be discussed as well as new research lines.

Salt transport in porous media: preliminary experimental and theoretical Analysis of salt diffusion

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ABSTRACT

Damage of building materials and building structures has a significant economical and ecological impact worldwide. Salt damage is a multi-factor problem, resulting from the interplay between the nature and structure of the porous object, the physical and chemical behavior of the salt solution, and the environmental conditions. Moisture plays an important role as the transport medium for salt in porous building materials.

Moisture and especially salt transport and crystallization in pores are widely recognized as one of the primary causes of the deterioration of porous building materials and in the conservation of historic buildings. In cold climates, like Portugal, sodium chloride can lead to durability problems when the building structures are exposed to marine environment. Various experimental methods have been developed to measure salt diffusion, some methods are based on Fick's law and use a "diffusion cell" and others on the Nernst-Planck equation and use a "migration cell". The main purpose of the work is to describe and illustrate the use of a new method to measure molecular diffusion coefficients which is applicable to all porous building materials. In the theoretical analyze, we consider a vertical column containing a building material specimen, and filled with liquid to some level above the top of the specimen (liquid "pool"). If a concentrated salt solution is then poured into this liquid "pool", with uniform concentration, the tracer will gradually penetrate down the building material sample. The concentration of tracer in the liquid "pool" decrease gradually in the time, until a uniform concentration of tracer, equilibrium, is reached in the whole liquid. Analysis of the process of salt diffusion may be made in analogy with the process of diffusion from a stirred solution of limited volume. Values of the "effective" molecular diffusion coefficient were obtained for different building materials, at temperatures between 5 °C and 45 °C. The results show that the increase in temperature resulted in an increase in molecular diffusion coefficient.

The experimental results obtained are in good agreement with the theoretical values of molecular diffusion coefficient presented in literature. Empirical correlations are presented for the prediction of "effective" molecular diffusion coefficient over the entire range of temperatures studied.

Influence of limestone microstructure on gypsum crystallization

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ABSTRACT

In this study, we describe the use of high resolution X-ray CT (HRXCT) combined with thin section microscopy and SEM-EDS to investigate weathering patterns inside two different limestone facies due to gypsum crystallization. The combination of both techniques allows to obtain a time lapse visualization of those specific disintegration processes. The objective was to compare the visualized and quantified weathering patterns inside the rock with its microstructure. The study focuses on the micromorphology of two time equivalent (Eocene) natural building stones, the Belgian Lede stone and the French Noyant limestone, and the susceptibility of the rock forming components (bioclasts, cement, matrix, etc.) to gypsum crystallization. Both Lede stone and Noyant limestone contain a significant amount of bioclasts, especially foraminifera. In order to predict weathering phenomena and their process rates, first, the role of the microstructure has to be investigated. Most literature provides general weathering rate process information but is less focussing on specific features of the stone. On the other hand, Fronteau et al. (2010) already illustrated the relationship between building stone microfacies and morphology of the lower layer of the sulphated encrusting on the Euville, Savonnières and Courville limestone and thus underlined the importance of the microstructure of the stone [1].

The microscopic texture of the Lede stone can be described as a laminated packstone and a bioclastic packstone or grainstone without structure. The porosity of the stone is very heterogeneous (4-10 %) due to a varying macroporosity of dissolved fossil fragments. Commonly, the fossil fragments in Lede stone are bivalves, gastropods and foraminifera. The latter belong mostly to the subgroup Miliolina and Rotaliina (*Nummulites*). The stone contains 40-70% of quartz grains and is cemented by a micritic-microsparitic cement. The Noyant stone is an almost pure very porous limestone (up to 45 % porosity) with a micritic matrix and contains, similar to Lede stone, a high percentage of fossil fragments (Miliolina). Furthermore, some dispersed, sub-angular quartz grains are present.

In this study, sulphated encrustations were obtained on both Lede and Noyant stone in laboratory after an induced strong acid test. The reader is referred to [2] for further details. Basically, the samples were put in an acid environment according to the European Standard NBN EN 13919 (2003) for 21 days. At the bottom of the recipient, a mixture of 500 ± 10 ml H_2SO_3 and 150 ± 10 ml de-mineralized H_2O was added. The cylindrical samples of both Lede and Noyant fine stone were scanned with HRXCT before and after the weathering test. SEM/BSE-EDS was performed on the final failed rock samples.

For the Lede stone, a relatively thick, external gypsum crust is visible on the thin sections and a preferential infilling is obtained in the wall structures of the foraminifera (Miliolina) and shell fragments after the exposure to an acid environment. In general, it is observed that the microsparitic cement around the fossil fragments is more resistant than the wall structure of the Miliolina. When looking to a differential volume of the CT-scan made before and after weathering, the same weathering patterns are visible. Figure 1 shows a reconstructed slice before and after weathering and a differential image. The latter reveals the places where gypsum was crystallized in micro-pores and on the surface (white) and where new pores were formed due to dissolution of calcium carbonate (black).

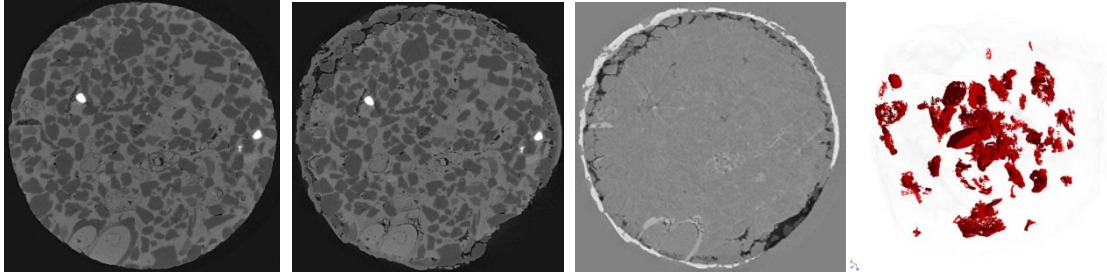


Figure 1: X-ray CT image before acid test (1), after acid test (2), differential image (3) and 3D rendered volume of gypsum crystallization inside the Miliolina fragments (4). On the differential image, the new pores (black) and gypsum (white) are visible. Diameter of the core is 1.6 mm.

The segmented volume reveals the location of gypsum inside the stone in 3D and as can be seen on figure 1, the gypsum concentrates inside the Miliolina and shell fragments (red). Their shape can easily be distinguished thanks to the complete recrystallization of calcium carbonate into gypsum. The highly porous wall structure of the Miliolina favors the crystallization of gypsum. On the other hand, the *Nummulites* show almost no recrystallization because of their hyaline, non-porous walls. A totally different weathering phenomena is observed for the Noyant stone. A thick weathering crust ($\pm 300 \mu\text{m}$) of gypsum and recrystallized calcium carbonate was detected. The highly porous micritic matrix was completely deformed by cracking as can be seen on the X-ray CT slices before and after the test (figure 2). Registration of the volumes was impossible due to this severe deformation. As the BSE-EDS images show, only Miliolina at the surface of the samples were attacked and others are only partially transformed or show no conversion into gypsum.

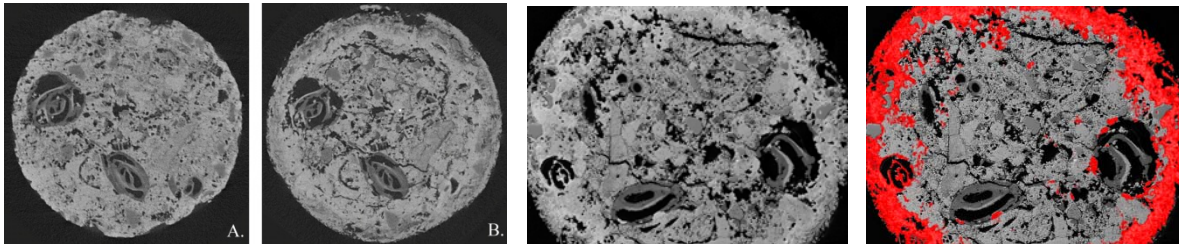


Figure 2: X-ray CT slice before and after weathering (left; A and B) and BSE/EDS image of a weathered Noyant stone (right) the gypsum is shown, in red. Diameter of the core is 1.6 mm.

The highly micro-porous micritic matrix of the Noyant stone made it more sensitive to recrystallizations than the bioclast present within the stone. On the contrary, the bioclasts (Miliolina and shell fragments) in the Lede stone were less resistant to weathering than the cement of the stone, resulting in internal preferential crystallization spots. The knowledge of the influence of the microstructure, including porosity, reactive surface and roughness is of prime importance in the understanding of the crystallization patterns. In addition, this approach illustrates that the characterization and prediction of weathering of natural building stones due to gypsum benefits of the combined use of thin section microscopy, BSE/SEM-EDS and X-ray CT.

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Effects of NaCl and NaNO₃ on the capillary suction, drying kinetics and vapour permeability of three building stones

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ABSTRACT

Salt decay is closely related to drying of porous materials, not only as a consequence but also because the salts are an influencing factor in drying processes. This influence, however, is not yet totally clear, as are not in general the effects of soluble salts on liquid and vapour transport through complex pore networks such as those of porous building materials.

Here, we analyse the role of two soluble salts, NaCl and NaNO₃, on the capillary suction and drying kinetics of three natural stones. The physical morphology of the efflorescence layer occurring in each case and the effect of such layer on vapour transport are also analysed.

Sodium chloride and sodium nitrate are among the most common salts in decayed buildings and also, particularly sodium chloride, two of the most used in laboratory experiments. Despite of their distinct composition, their equilibrium relative humidity is similar: 75.47% for NaCl and 75.36% for NaNO₃ at 20°C [1]. Four solutions with different concentration were tested in the case of NaCl and three in the case of NaNO₃.

The natural stones were the Bentheimer sandstone (B) and two Portuguese limestones that correspond to the Ançã limestone (CA) and a current limestone of lower porosity (CC).

The experiments followed RILEM procedures [2] and consisted on performing sequentially, on the same specimens, the following three types of test: determination of the absorption coefficient with water and the salt solutions, measurement of the evaporation curve, and determination of the coefficient of water vapour conductivity of the uncontaminated and salt contaminated specimens.

As regards the influence on liquid capillary transport, the results show that, for the three stones, the sorptivity of the salt solutions scales precisely as $(\sigma/\eta)^{1/2}$, where σ is the surface tension and η the viscosity of the liquid, as predicted theoretically [3]. The greatest sorptivity reduction occurs thus for NaNO₃: the values for the saturated solution are around 60% of those obtained for pure water, whereas for NaCl they are around 70%.

In relation to the drying kinetics, although for the concentrations closer to saturation the differences are sometimes less clear, a general trend can be observed: the higher the salt concentration the slower the drying. However, some isolated specimens deviate from this general trend, depicting a markedly slower drying kinetics. There were occurrences for the three materials and the two salts, which have an apparently random nature: the drying curves of the affected specimens diverge suddenly, triggered by some unidentifiable event or character.

At the end of drying, a layer of efflorescence was observable on the surface of the specimens. Its morphology was often similar for the two salts but varied significantly with the type of stone. As revealed by optical microscopy:

- CA developed thick crusts of vertically oriented crystals, apparently more compactly packed for the chloride than for the nitrate;
- CC presented shrivelled NaCl salt crusts which possessed holes at most of the hills and occasional fissures; the holes tend to develop at areas where dark clasts are present on the stone surface, which should correspond to a less porous mineral; for NaNO₃, most surfaces were covered by a porous coat of whisker-like efflorescence.
- B developed nodules of cauliflower-like efflorescence lying on a thin vitreous coat of salt; the two specimens which had much slower drying showed a different efflorescence morphology consisting on a thick and compact vitreous layer.

The vapour permeability of the efflorescence-covered materials, overall, decreases linearly with the concentration of the salt solution used, i.e., with the thickness of the efflorescence layer. The changes, however, are mostly irrelevant in all cases except for CA with sodium chloride. This difference seems to be closely related to the morphological characteristics, and particularly the porosity, of the efflorescence layer. What probably happens is that for CA with sodium chloride the efflorescence layer is compact enough to significantly disturb the transport of vapour. In all the other cases the porosity of the

efflorescence layer is higher, either because the packing of the crystals is less compact or because the salt crust possesses holes and fissures, therefore, there is not much influence on vapour transport. In general, the variations in drying kinetics are consistent with the differences in vapour permeability or efflorescence morphology, inclusively in the cases of the specimens with random deviant behaviour. Summarizing, the work done until the present moment indicates that:

- The changes induced by soluble salts in capillary transport are due to their effect on the surface tension and viscosity of the liquid and are proportional to $(\sigma/\eta)^{1/2}$, as predicted theoretically.
- The vapour transport hindering effect of salt deposits is very dependent on the habit and packing of the crystals. This was observed for external salt deposits (efflorescence crusts) but it is logical to expect that a similar effect may happen at the pore level, i.e., for internal deposits (subflorescence).
- Compact crusts of salt may relevantly hinder the passage of vapour. However, porous efflorescence layers with a negligible influence on vapour transport are probably also frequent. The difference between the two types is not easily detected by the naked eye and can be elusive in current site observations.
- Efflorescence morphology depends on factors such as the type of salt and the characteristics of the porous material, as previously concluded also by other researchers. However, it seems to incorporate also random causal factors, which may prove to be ultimately significant, probably derived from small casual inhomogeneities in the environmental conditions or in the complex pore network of the building material.

Acknowledgements

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Thursday, September 06, 2012

8 : 3 0 - 9 : 1 0	<u>Michael Steiger</u> and Kirsten Linnow	Keynote lecture 4 - Hydration reactions in confinement: salt hydrates in porous materials for thermochemical heat storage
9 : 1 0 - 9 : 3 5	<u>P. A. J. Donkers</u> , J. F. M. van Rens, L. Pel and O.C.G. Adan	Na ₂ SO ₄ , the first step to thermo chemical heat storage
9 : 3 5 - 1 0 : 0 0	Inge Rørig-Dalgaard	Determination of the deliquescence point in salt mixtures by utilizing the dynamic vapour sorption method
1 0 : 0 0 - 1 0 : 2 5	<u>Kirsten Linnow</u> and Michael Steiger	Experimental studies of the mechanism and kinetics of hydration reactions
1 0 : 2 5 - 1 0 : 5 5	Coffee break	
1 0 : 5 5 - 1 1 : 3 5	José Delgado Rodrigues	Keynote lecture 5 - Salts in stone conservation. From insidious enemies, to transient friends and inconvenient neighbors
1 1 : 3 5 - 1 2 : 0 0	<u>Berta Mañas Alcaide</u> , Xavier Mas-Barberà and Stephan Kröner	Differences in poulticing behavior depending on materials and application techniques
1 2 : 0 0 - 1 2 : 2 5	<u>Roel Hendrickx</u> , Hilde De Clercq, Sebastiaan Godts and Chiara Giannotti	A moisture transport-based approach to estimate the effect of desalination poultices and salt accumulating renders
1 2 : 2 5 - 1 2 : 5 0	<u>Sebastiaan Godts</u> , Hilde De Clercq, Roald Hayen and Roel Hendrickx	The crystallization of salt mixtures in relation to a climate study to mitigate salt decay in Medieval Murals and Limestone Tracery
1 2 : 5 0 - 1 3 : 5 0	Lunch	
1 4 : 0 0	Gathering at the hotel lobby	
1 4 : 1 5 - 1 5 : 0 0	Walk to Tróia marina (through the beach)	
1 5 : 0 0 - 1 8 : 0 0	Boat tour with dolphin watching	
1 9 : 3 0 - 2 0 : 3 0	Aperitif at the bar	
2 0 : 3 0	Dinner	

KEYNOTE LECTURE

Hydration reactions in confinement: salt hydrates in porous materials for thermochemical heat storage

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ABSTRACT

Many salts occur in different hydrated forms and hydration reactions are generally considered as important causes of damage in construction materials or natural rock. Hydration–dehydration equilibria are also of increasing interest due to the use of salt hydrates as thermochemical heat storage materials. Such a thermochemical system is based on the release of the heat of hydration. A salt hydrate storage system is charged by the endothermic thermal dehydration of the higher salt hydrate. Many salts can be dehydrated at temperatures that can well be achieved using solar thermal collectors. In this state, the energy can be stored over long periods of time implying its application for seasonal storage. The exothermic back reaction may be initiated by simply increasing the water vapor partial pressure. The hydration–dehydration equilibrium of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ is one promising example with a very high theoretical energy density for both seasonal and short term energy storage.

The performance of a salt hydrate storage system largely depends on the kinetics of the hydration and the dehydration reactions. Such reactions are solid state reactions, hence, they are slow and often they are under kinetic control. In effect, hydration–dehydration reactions of most salts are characterized by the formation of metastable phases. In order to predict the behavior of a particular salt, a complete phase diagram including stable and metastable phases is required. There are different approaches to optimize the kinetics of hydration reactions including the addition of hygroscopic salts and the use of composite materials of a porous substrate carrying the salt hydrate.

The dispersion of crystals to submicrometer size in porous substrates offers the advantage of a significantly increased crystal surface area available for gas–solid heterogeneous reactions. In addition, using nanoporous materials increases the overall heat effect by increasing the heat of hydration of the embedded salt by the heat of sorption of the porous substrate. However, it is well known that crystal growth during hydration reactions in porous substrates generates substantial stress. Therefore, a complete phase diagram to predict the hydration–dehydration behavior of salts needs to consider the pressure dependence of the phase equilibria. It is also well known that the pressures generated by confined growing crystals in a hydration reaction are substantial and may exceed the tensile strength of many materials. In the case of energy storage, a high tensile strength is an important property of a suitable host material with high cycle stability. In the case of construction materials, very often the tensile strength is not sufficient and the pressure generated in hydration reactions causes severe damage. The origin of this pressure is sometimes subject to controversial discussion and is attributed to both hydration and crystallization pressure.

In this talk, we will discuss the theory and experiments to establish the phase diagrams of salt hydrates and to assess the influence of pressure on the phase equilibria. The pressure dependence also includes the treatment of the thermodynamic background of hydration and crystallization pressure and their relevance for understanding damage in construction materials.

Na₂SO₄, the first step to thermo chemical heat storage

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ABSTRACT

Systems that buffer energy are needed to match the demand and supply of renewable energy. There are several ways to store energy; one of the most promising systems is based on thermo chemical energy. This system uses the energy release of a chemical reaction. For heat storage application this system is profitable, because this reaction is reversible.

One particular heat storage method with a high potential makes use of the crystallization energy of salts. The reaction is given by:



where A is a salt, some promising salts are MgSO₄, CaCl and LiCl; B is a solvent, mentioned in literature are H₂O, NH₃ and CH₃OH and AB is the salt crystal of A and B. The heat generated by this reaction depends on the salt-solvent combination, but can be in the order of 500 kWh/m³. This means that by picking a good combination of salt and solvent a system of 10 m³ can store your energy consumption of a whole year! A drawback of the system is that by cyclic crystallization-decomposition of the salt systems the efficiency decreases^[1].

Here we have used NMR to get more information on the crystals during cyclic reactions. To this end we make use of a 4.7T magnet, as to be able to measure at very low moisture contents. A special insert was designed to control the temperature of the sample and to measure simultaneously the mass of the sample. The relative humidity over the sample can be changed within a range of 0-98% RH. Special attention was given to the Bird-cage design as to be able to measure short relaxation times, i.e., to distinguish on basis of relaxation analysis which is free and hydrated water.

As an example in figure 1a the measured moisture profiles of a dehydration experiment are given for a sample filled with Na₂SO₄·10H₂O crystals. Air is blown over the sample with a relative humidity of 0%. These preliminary results already show that a sharp dehydration front is observed. In figure 1b we have also given the results for various measurements with different crystal sizes. These results show that for large crystals the dehydration is faster in time. In the near future we want to use this information for modeling the reaction processes in these reactors during cycling.

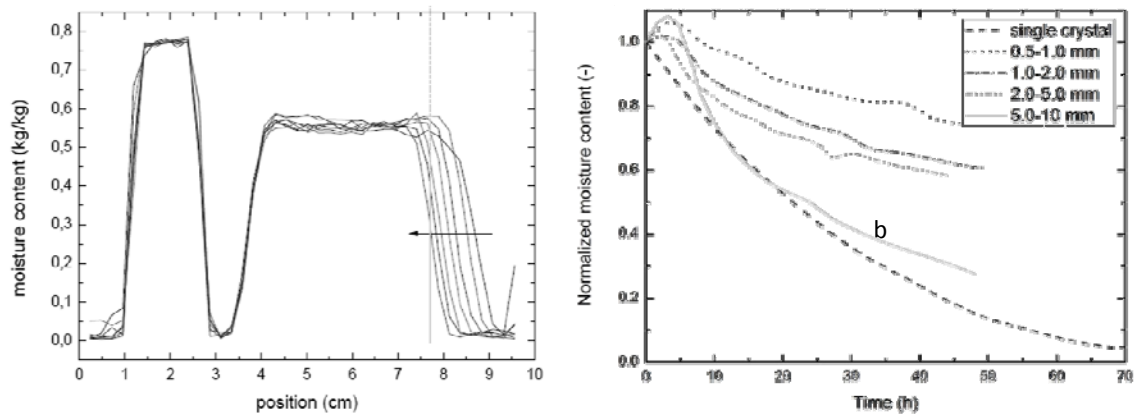


Figure 1a: The moisture content profiles of the dehydration experiments of Na₂SO₄ with grain size of 0.5-1.0 mm. The time between 2 plotted profiles is 8 hours. Figure 1b: The normalized moisture content plotted against the time for different grain sizes of Na₂SO₄.

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Determination of the deliquesce point in salt mixtures by utilizing the dynamic vapour sorption method

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ABSTRACT

Background and objectives

Salts are generally recognized to be one of the main courses for deterioration of porous materials. The damage and eventual removal of the salt is dependent of whether the salt is crystallized or dissolved. In relation to desalination of church vaults for future preservation of the murals it is of interest to limit the applied liquid during the desalination e.g. to prevent drying cracks and creating conditions for microbial growth [1]. At present climate chambers with a specific temperature and relative humidity are used to prevent salt induced deterioration and also in this relation it is of interest to find the deliquescence point since the relative humidity can be kept on the most effective level without causing damage. The deliquescence point for single salts is well known; however, in case of salt mixtures the combinations are comprehensive. In order to find deliquescence points for specific salt mixtures different simulation programs have been used as e.g. RUNSALT [2], ECOS [3], however several assumptions have to be made and therefore these programs are by several considered as limited reliable. In [4] phase diagram for the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system was calculated on basis of thermodynamic data as a function of temperature. In [5] a model approach was made to predict phase equilibria in case of salt mixtures and safe ranges of environmental conditions taking temperature, varying ions, moisture contents and activities into account. The model was based on the semi-empirical model from Pitzer where some parameters were experimental determined. The results were given in RH as a function of temperature. In order to understand the fundamental mechanisms such a model as deduced in [5] is essential. The need for incorporating the transport properties of the porous material and dissolution and crystallization kinetic of the various salts is mentioned to be strongly depended to the transport properties of the various salts in reality [5]. Measurements of the deliquescence point and the kinetics for some specific salt mixtures in materials at a specific temperature would further contribute to the understanding of salt mixtures and this is the content of the present work by utilizing dynamic vapor sorption method (DVS).

The Dynamic vapor sorption method

The deliquescence point can empirically be found by producing water vapor sorption isotherms which previously were found by time and labor intensive desiccators and saturated salt solutions. A further development of the original water vapor sorption isotherm method is the dynamic vapor sorption method (DVS). The DVS method is a gravimetric technique measuring the velocity and the extent to which a solvent is absorbed by a sample. In a DVS experiment this is accomplished by exposing a sample to a series of step changes in relative humidity and monitoring the mass change as a function of time. The sample mass must be allowed to reach gravimetric equilibrium at each step change in humidity before progressing to the next humidity level. Then, the equilibrium mass values at each relative humidity step are used to generate the isotherm. The DVS method has previously been used for identifying a stable crystalline salt in order to allow clinical development activities. During this work a hysteresis effect was measured when exposed to high humidity's which they propose was caused by a change from an anhydrous salt to a more hydrated salt [6].

Expected results

The DVS will be used to determine the sorption isotherm for NaCl (for comparison with reference values), $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ (for comparison with [4]) and salt mixtures taken from three different positions from the vault of Rørby Church, Denmark (to be used during future desalination). On basis of the results which are to be measured in august 2012, it will be discussed whether satisfactory results can be obtained with the DVS method for determination of the deliquescence point in relation to salt mixtures at a specific temperature.

It has to be discussed whether it is of interest to determine a precise deliquescence point of a salt mixture in practice or whether the deviation between the three taken samples in Rørby church makes such a precise determination meaningless.

Also in case of establishing a climate chamber to prevent further salt induced deterioration a RH could be chosen to the climate chamber on basis of determination of the deliquescence point in a limited temperature

intervals. Since temperatures are most often recorded in advance to desalination the deliquescence point at one specific temperature would give valuable information.

In a previous work the known value for the deliquescence point of the single salt NaCl was confirmed by very primitive measurements in a microclimate and it was shown that in case of dissolved ions (and possibly a limited contribution from the compress plaster) a high desalination efficiency was obtained by use of a new electrokinetic method [7-9].

Acknowledgements

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Experimental studies of the mechanism and kinetics of hydration reactions

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ABSTRACT

The mechanism and kinetics of hydration reactions are not only important to understand the pressure exerted in confined space but also for the application of a salt hydrate as thermochemical heat storage material. Sodium sulfate and magnesium sulfate monohydrate were chosen in this study because they are both promising as thermochemical heat storage materials due to their high theoretical energy density of $2.2 \text{ GJ}\cdot\text{m}^{-3}$ and $2.4 \text{ GJ}\cdot\text{m}^{-3}$, respectively. Moreover, it is well known that both salts cause severe damage of building materials. Hence, they are often used in durability tests of building materials, such as the ASTM aggregate sound test.

Hydration reactions under several climatic conditions were observed by using Raman microscopy. It turns out that during the hydration at higher humidities droplets of solutions saturated with respect to the lower hydrate are formed which are supersaturated with respect to the higher hydrated phase and subsequently crystallization takes place. As an example the hydration of thenardite at 92% RH and 23°C is shown in Fig. 1. After one hour exposure time (Fig. 1a) small thenardite crystals were dissolved (arrow) while larger crystals remained as thenardite and the formation of mirabilite was not yet observed. Two hours later the large crystals (arrows in Fig. 1b) were hydrated to mirabilite whereas medium sized crystals dissolved. In the interior of the large droplet (Fig. 1b) thenardite is clearly visible and was identified by Raman spectroscopy. Shortly after the droplet got in contact with the mirabilite particle spontaneous crystallization of mirabilite occurred, thus providing clear evidence for crystal growth from a highly supersaturated solution. After 6 hours some droplets were still present and all crystals shown in Fig. 1c consist of mirabilite.

At low humidities hydration reactions are significantly slower and neither visible solution nor the Raman spectrum of a sulfate solution was found. In addition water vapor sorption experiments were carried out and hydration rates were determined. The experimental observations are discussed on the basis of the well known $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ phase diagrams. It turns out that the hydration rate increases with increasing humidity. However, above the deliquescence humidity of the lower hydrate a through solution mechanism takes place further accelerating the water uptake.

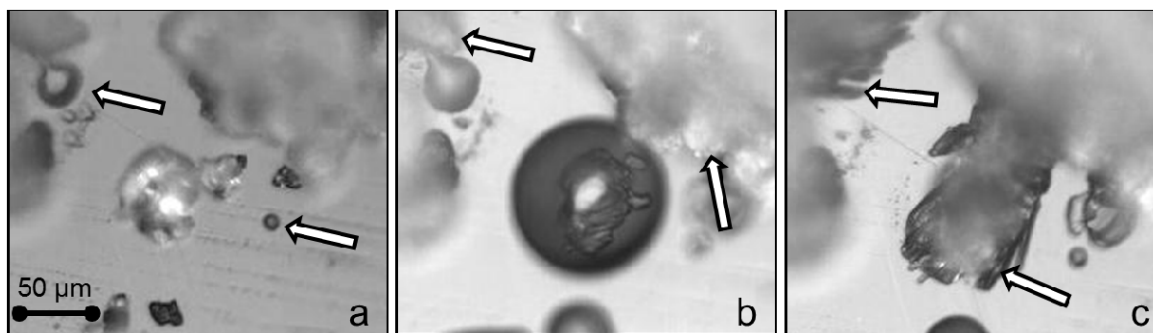


Figure 1: Hydration progress of thenardite at 92% RH and 23°C after exposure times of (a) 1h 47min, (b) 3h 16min and (c) 6h 6min.

KEYNOTE LECTURE

Salts in stone conservation: From insidious enemies, to transient friends and inconvenient neighbours

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ABSTRACT

Salts are well known deterioration agents [1] and are widespread in our constructions. Sulphates, chlorides, nitrates and carbonates represent the most frequent anions, but others less frequent such as phosphates and oxalates can be found. They combine with cations to form a very large number of mineral species, the real entities that we find in our walls. They can be seen popping up at the surface, or staying concealed below it, or just moving up and below, as the weather conditions determine. There are typical places to find them in good amounts [2], best seasons to harvest, established methods for tracking them, but they can be found anywhere, and nowhere is absolutely safe from them. They may be circumstantially associated to many other entities, but only water can be considered as a constant companion to them. And they move around, in our constructions. Sometimes the occurrence patterns inform where they come from, the composition may be an indication of their birthplace, but it is hardly feasible to guarantee which paths they have followed and how they have interacted during their journey. They may be strong fighters and highly destructive warriors, or be simple aesthetic disturbing presences, but they are never totally innocuous and irrelevant. A disturbing agent that can be found everywhere, uses camouflage strategies, may have multiple origins, characters and movements is, in fact, a very **insidious enemy** that demands to be carefully considered and counteracted.

And yet, salts are one of the most praised and recurrent ingredients of researchers and scientists [3]. From Brard [4] and Thomson (1862) [5] (quoted from Honeyborn (1965)[6], to modern researchers, salts have been a work material and their role an intriguing problem, but apparently a very frequent cherished source for curricula nourishment. Salts are instrumental to help testing materials (RILEM [7], ASTM [8]) and to decide whose to be accepted or to be rejected. They may serve as a stressing agent to newly treated specimens to force treatments to demonstrate how good or how bad they are for the stone [9]. And they may even help us to prepare our specimens to more accurately mimic aged materials to obtain samples adequate to serve as working materials in our experiments [10]. It is not simple to understand what they cause and what the results mean, but this is our fault, and in this aspect these **transient friends** are not to be blamed for.

In the daily practice in stone conservation, we have almost always to assume that “they” are there. They are in that large band parallel to the ground that runs along most of the ground level. They are also high in the wall near those uncared windows, below those broken tiles of the roof. And in that degraded vault over the transept, and in those recently repaired joints. They are threatening the remains of the original mural painting, and are waiting to bursting out below those ugly black crusts. It is not question to avoid them. They arrived there before us. And it is not question to eliminate them completely either. We need to learn how to “live” with them. We may consider eliminating part of them and keeping their amount at a safer level. We may command where we want them to stay by managing properly an overlying plaster cover [11]. And we may consider eliminating them superficially to allow us to treat the decayed stone in a safer way [12,13].

We know for sure that water is an inseparable companion and a critical logistic factor for salts. They may look unpleasant, but without water they are almost harmless. So, knowing how difficult is to defeat them, move your efforts to take water away from them. Repair those leaking points, avoid conditions for condensation, install a damp proof courses, and any other tricks to keep them with dry “feet” as far as possible. They may offer nice fluffy crystals that may give an erroneous feeling of peaceful actors, but in fact they are not companies to be recommended and have to be considered as permanent **inconvenient neighbours**.

Starting from illustrations of damage situations induced by salt crystallisation, the presentation will discuss a few examples on laboratory use of salts for testing purposes, ending with a few examples of practical applications of conservation actions is salt laden objects.

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Differences in poulticing behavior depending on materials and application techniques

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ABSTRACT

The presence of soluble salts and water, among other circumstances, in porous building materials, is considered one of the most harmful causes of stone decay on cultural heritage [1, 2]. This decay is produced by different mechanisms that have been widely studied during last decades [1, 3 and 4].

When soluble salts and water presence produce a decay of support and/or polychrome, it is necessary to apply a treatment that mitigates or paralyzes the decay. Treatments used for this purpose are: methods for insolubilizing salts, modification of room humidity and temperature, and partial or total desalination of the support. Desalination treatments are numerous, and can be grouped in two types depending on their applicability: those which can be applied on small and/or detached works of art, and those applicable on any kind of work of art.

Drying poultice is a common technique used by restores for salt extraction to reduce soluble salts levels in porous materials that can be applied on any kind of work of art. This method is relatively easy: the poultice is made of one or more hydrophilic materials mixed with water and other substances, which is placed over the porous material for a certain time before being removed. Many authors have referenced that desalination by poulticing has two phases: a) the first one of support humectation where water gets into the porous system of the support, solving soluble salts, and b) the second phase of support and poultice drying where soluble salt extraction takes place [5-7].

The physical principles that take place on desalination treatments by poulticing are diffusion during the first phase of humectation and, diffusion and mainly advection during the second phase of salt extraction [5, 6, and 8]. Depending on salt transport process, other conditions are necessary to perform an effective salt extraction.

Based on the latest investigations about physical principles of the salt and moisture transport, this research studies the different behaviors depending on the porosity and pore size distribution of support and poultice, application techniques and poultices materials.

This study compares the results of the extracted salts (amount and maximum extraction depth) with three different kinds of poultices, on two types of natural stone with a great difference in porosity and pore size distribution. Other variables commonly performed on salt reduction treatments by dry poulticing have been fixed in order to reduce alternatives. These variables are the type of soluble salt added (NaCl), the thickness of the poultice (0.5 cm), the time of contact (48 hours) and the number of applications (3).

Six test specimens have been analyzed: three of Tosca Rocafort (travertine) and three of Bateig Novelda (biocalcarene). All the test specimens were previously desalinated by several deep immersions in deionized water. A saturated solution of 360g of NaCl per liter of water was prepared and stone test specimens were immersed during 10 days. Three types of poultices were applied: a thin porous poultice (sepiolite), a mixed porous poultice (sepiolite and glass) and thick-thin porous consecutive poultices (cellulose powder-sepiolite).

A considerable amount of samples from support and poultices have been analyzed. Samples on support were taken at five depths (0-0.5 cm, 0.5-1.5 cm, 1.5-3 cm, 3-4.5 y 4.5-6 cm), before saturation with NaCl, after salt saturation and after each of the three poultices applications. Poultices applied on the six test specimens after each of the three applications were also measured.

The quantitative content in soluble salts was determined by ionic conductivity following the procedure described at the Italian Norma UNI 11087-novembre 2003 [9].

The main objective of this research is to compare the behavior of these three different poultices on different stone materials. Differences in behavior may be explained because of the relation between the support and the poultice porosity. The experimental part of this research is still going on and sampling measures have not been finished yet. Results of this sampling will be ready by the end of May 2012. As long as main results are established and studied, conclusions will be ready by the end of June 2012.

Acknowledgements

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A moisture transport-based approach to estimate the effect of desalination poultices and salt accumulating renders

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ABSTRACT

This contribution presents the on-going investigations at KIK-IRPA to estimate the effects of desalination poultices and salt-accumulating renders (or plasters) on salt contaminated porous substrates. The working principle of both types of materials is based on the absorption of liquid water into the substrate (ceramic brick) and the subsequent dissolution of salt crystals present, followed by the reverse transport towards the new layer(s) during drying. The physical principles were investigated in [1], [2] and [3]. However, in current practice the effectiveness is still generally assessed by either in-situ trials [4] or replica-experiments in the lab.

The two key parameters for poulticing are: the depth over which salts are removed, the quantity and the required time of application. Another important question is whether the substrate should be pre-wetted and how much. A larger timescale applies for salt accumulating renders (typically several years) for which the goals are slightly different. Ion transport towards the render may be a rather long-term wicking-like process where the moisture and salt source is typically the soil behind or below the wall. The efficiency of the application depends on the position of the drying front and the evaporation rate at this front.

The investigation carried out at KIK-IRPA is based on the theory of moisture transport and consists of three parts: (1) the experimental determination (on-site and in the lab) of relevant moisture transport parameters of substrates in practical cases, (2) the measurement (in the lab) of relevant moisture transport parameters of a number of commercial salt accumulating renders and (3) the numerical simulation of heat, moisture and salt transport in the combined system substrate-poultice or substrate-render.

In total 20 types of render and 2 types of poultices were investigated. The number of renders reduces to some 7 multilayer systems. Test specimens of these systems were produced for salt crystallisation tests. The selected test procedure is an interrupted wicking experiment. The material properties and the sequence of the layers were modelled in the simulation software.

The software used is Delphin 5, which is developed for heat- air and moisture (HAM) transport simulations, but which also contains a salt module which includes diffusion and advection, evaporation and condensation, hydration and dehydration and deliquescence of salts [5]. It uses the Pitzer model for ion and water activities. Osmotic pressure is not taken into account.

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The crystallization of salt mixtures in relation to a climate study to mitigate salt decay in Medieval Murals and Limestone Tracery

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ABSTRACT

As salts are commonly found in monuments, and particularly in industrial environments such as Liege (Belgium), the salt content found in the murals and limestone tracery of the 16th century main entrance porch from the Saint Jacobschurch in Liege has been investigated and evaluated in relation to the indoor climate conditions. The research includes the determination of the actual and hygroscopic moisture contents and the quantitative ion content of lifted samples, the prediction of their phase equilibriums and a climate monitoring for a period of 12 months.

While the deliquescence points and the conditions for damage of single salts are well documented, the deterioration processes in case of salt mixtures become considerably more intricate. For building materials contaminated with a complex mixture of ions, an understanding of the thermodynamics of their phase transitions is required to assess the critical environmental conditions and the potential risks of salt damage. The computer program ECOS/RUNSALT is capable of predicting the crystallization behavior of salt mixtures based on a thermodynamic approach [1][2]. From the data obtained by the quantitative ion analyses the computer model enables the user to determine ranges of temperature and relative humidity (RH) in which phase transitions are kept to a minimum. The ECOS/RUNSALT outputs can then be compared to the climatic conditions monitored in the main porch of the church to evaluate the potential risk of salt damage.

In the murals and limestone tracery gypsum was identified together with a mixture of sodium nitrate, sodium chloride and calcium nitrate. The crystallization of these salts (excluding gypsum) will occur at RH between 25 and 65%. The climate study reveals that conditions of approximately 30% RH are measured numerous times and during several hours in afternoons and early evenings in the summer, such that the crystallization of hygroscopic salts such as calcium nitrate – crystallizing only under very dry conditions – cannot be ignored. During periods of extreme drought, often not considered, hygroscopic salts can become an important factor in the decay of historic building materials.

The results of the scientific process and possible conservation methods are presented and contribute to formulate a mitigation strategy to prevent further salt decay of the murals and tracery. The results show that the required conditions for preserving the murals and the tracery in the porch are a RH of at least 65% and a temperature of 20°C. In these conditions the salts are constantly dissolved in ambient moisture and no salt transitions occur. Knowing the appropriate thermohygrometric ranges, the question remains whether these climatic conditions are feasible. Today, the indoor climate conditions of the church porch are almost equal to the external climate as a result of damaged leaded glass windows and the lack of thermal insulation under the saddle roof or beneath the stone floor. Furthermore, the porch is regularly left open during religious ceremonies. Apart from basic repairs such as preventing water infiltration, a building physical approach of the complete porch is required to formulate a proper implementation of thermal insulation requirements and recommendations concerning the future use of the porch. These measures will result in a more controlled climate and a mitigation of salt damage. Another approach includes the extraction of salts using poultice materials tailored to the properties of the salt contaminated surface, such as the pore size distribution [3][4][5]. This method could be applied on the limestone tracery. However, such an approach is not applicable to the murals, which contain an organic binder hindering the moisture transport.

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Friday, September 07, 2012

8 : 3 0 - 9 : 1 0	Encarnación Ruiz Agudo	Keynote lecture 6 - Physical and chemical mechanisms of salt weathering: combined strategies
9 : 1 0 - 9 : 3 5	<u>Leo Pel</u> and Tamerlan A. Saidov	Sodium sulfate crystallization in porous building materials due to drying
9 : 3 5 - 1 0 : 0 0	<u>Florian Osselin</u> , Antonin Fabbri, Teddy Fen-Chong, Arnault Lassin, Jean-Michel Pereira and Patrick Dangla	Poromechanics of the crystallization of salt during carbon dioxide injection in a deep saline aquifer
1 0 : 0 0 - 1 0 : 2 5	<u>Anna Ramon</u> and Eduardo E. Alonso	Thaumasite and ettringite massive crystal growth in two railway embankments
1 0 : 2 5 - 1 0 : 5 5	Coffee break	
1 0 : 5 5 - 1 1 : 3 5	Nima Shokri	Keynote lecture 7 - Pore scale investigation of the mechanisms governing evaporation from porous media
1 1 : 3 5 - 1 2 : 0 0	<u>Teresa Diaz Gonçalves</u> , Vânia Brito, Leo Pel, José Delgado Rodrigues	Magnitude of the stage I drying rate of porous building materials with different porosity
1 2 : 0 0 - 1 2 : 2 5	<u>W. de Boever</u> , W.V. Cnudde, J. Dewanckele, M. Boone, T. de Kock, M.N. Boone, E. Van Ranst, G. Silversmit, L. Vincze, H. Derluyn, P. Modregger, M. Stampanoni, K. de Buysser and G. de Schutter	Characterisation of sandstone (Kandla Grey) weathering behaviour by frost and salt action
1 2 : 2 5 - 1 2 : 5 0	<u>Rita Nogueira</u> , Ana Paula Ferreira Pinto and Augusto Gomes	Artificial weathering of lime mortars Desalination control by the drilling resistance measurement system
1 2 : 5 0 - 1 3 : 5 0	Lunch	
1 4 : 2 0	Bus transfer to Lisbon - boarding (the arrival times we estimated were: Airport – 16:50; LNEC – 17:15)	

KEYNOTE LECTURE

Physical and chemical mechanisms of salt weathering: combined strategies for preventing damage to porous materials

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ABSTRACT

Crystallization within the void spaces of rocks and man-made materials is considered a mayor physical weathering process, and it is relevant to nearly every field of science, from industrial concerns related to pipe clogging in heating, cooling and oil recovery systems, to pore blockage in CO₂ sequestration, cement setting, crystal growth in gels, biomineralization, and conservation of cultural heritage and modern constructions affected by frost and salt damage. Conversely, the possible role of salts in the chemical weathering of minerals has been generally neglected, and previous studies have failed to disclose any relation between chemical and physical weathering phenomena induced by salts. Here we present evidence obtained by a combination of experimental techniques such as Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Environmental Scanning Electron Microscopy (ESEM), on the chemical (dissolution) and physical (crystallization pressure) weathering induced by common and damaging soluble salts on a mayor rock-forming mineral such as calcite, and we propose novel strategies that may help preventing salt damage of porous materials by tackling both chemical and physical aspects of salt damage based on the formation of an organic (i.e. organophosphonate) nanofilm.

The results of our research show that, at high phosphonate concentration (> 5 mM), the reaction of calcite surfaces with phosphonates follows a pathway of dissolution of the substrate followed by precipitation of a calcium phosphonate phase. The presence of this overgrowth reduces calcite dissolution rate, thus representing a new treatment aimed at reducing solution-induced weathering of rock-forming minerals. As well, our results demonstrate that these additives act as crystallization promoters of inorganic salts on calcitic substrates, an effect that results in a (measured) decrease in the critical supersaturation reached by these salts when crystallizing in confined geometries, i.e., a pore, thus resulting in a reduction in crystallization pressure and damage to porous substrates such as building stones.

These results have implications in fields where in-pore crystallization of salts results in damage or plugging of the porous network, e.g., cultural heritage conservation and in the oil industry, where phosphonates are used as crystallization inhibitors.

Sodium sulfate crystallization in porous building materials due to drying

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ABSTRACT

Sodium sulfate is known as one of the most destructive salt leading to the deterioration of porous materials such as, monuments, sculptures and civil engineering structures. While sodium sulfate crystals are growing in a porous material a crystallization pressure will built up. The three main crystalline phases which can be formed are: thenardite (Na_2SO_4 , anhydrous salt), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and the thermodynamically metastable heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$). In order to predict and prevent crystallization damage it is necessary to know the salt phase that is responsible for damage as well as its nucleation and growth behavior in a porous material. In this study we have used Nuclear Magnetic Resonance (NMR) to non-destructively measure the concentration in materials during drying. We have combined the non-destructive measurement of the concentration of the pore solution in a material by using Nuclear Magnetic Resonance (NMR) with optical measurement of the dilation of the material during crystallization, giving the possibility to study the expansion due to crystallization. It was observed that for all studied materials thermodynamically metastable heptahydrate rather than the stable mirabilite is being formed.

Poromechanics of the crystallization of salt during carbon dioxide injection in a deep saline aquifer

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ABSTRACT

In the context of increasing environmental concern, Carbon Capture transport and geological Storage (CCS) appear to be an interesting solution to cope with global warming and increasing carbon content in the atmosphere. However, development of the deep saline aquifer storage requires additional research and development particularly in physics of porous media and coupled processes. Indeed, injection of supercritical carbon dioxide in a deep saline aquifer disturbs dramatically the equilibrium of the medium leading to highly coupled THMC (Thermo-Hydro-Mechanical-Chemio) behavior. For instance, numerical simulations have shown the strong effect of the precipitation induced by carbon dioxide injection on the porosity and permeability. Indeed, by adding solid matter in the porous medium, precipitation decreases porosity, which has a huge impact on permeability by clogging the percolating paths. A few percent decrease of porosity can often lead to a drop of several orders of magnitude in permeability [1].

On the other hand, it is known since Correns (see [2] for a commented translation of the original paper), that crystallization of salt in a porous medium is the cause of the creation of strong stresses on the pore wall, able to fracture and damage the porous medium. This mechanical effect named crystallization pressure, which is commonly not considered in CCS studies, may lead to counteract the diminution of injectivity by creating a connected micro-fracture network. This also arises several security issues because the damage on the host rock may open leaking paths that can be detrimental to the adjacent environment.

The aim of our work is to determine the balance between clogging and damage in order to predict the evolution of porosity and permeability during carbon dioxide injection at the material scale. The study presented here is based on both experimental and theoretical work. At first an updated expression of the so-called Correns law [4] has been developed taking into account temperature and pressure variations, and then a microscopic model has been obtained in order to calculate the creation and evolution of crystallization pressure in a representative elementary volume using the poromechanical framework developed at Laboratoire Navier (cf. Figure 1).

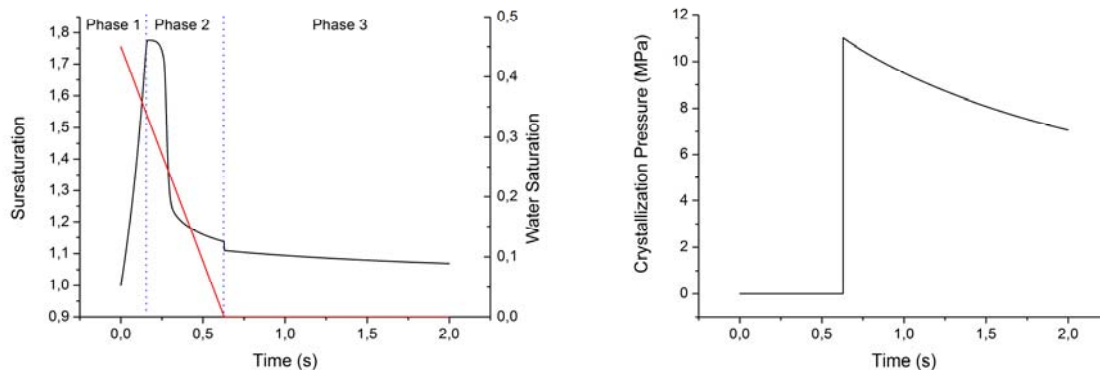


Figure 1: Evolution of sursaturation (left) and crystallization pressure (right) in a pore subjected to flow through drying

This theoretical work is conducted in parallel with an experimentation of reactive percolation allowing the injection of supercritical carbon dioxide in a plug of rock saturated with brine, and under geotechnical conditions (temperature and triaxial stresses). The aim of this experiment is to give an insight of the evolution of porosity and permeability during the carbon dioxide injection, conjointly to results on the crystallization pattern and porous matrix evolution in order to determine the relative importance of both clogging and damage.

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Thaumasite and ettringite massive crystal growth in two railway embankments

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ABSTRACT

Thaumasite and ettringite crystal growth is at the origin of an intense expansion that affected two embankments, 18 meters high, located in the Madrid-Barcelona high speed railway. The embankments were made of compacted sulphated Tertiary claystone. The embankments material belongs to the same geologic formation where Lilla tunnel [1] and Pont de Candí bridge [2], [3], have experienced severe heave problems due to gypsum crystal growth.

Pallaessos embankments give access to a bridge 196 meters long. A transition wedge was built next to abutment structures in both embankments in order to provide a progressive change of stiffness when trains approach the rigid bridge structure. Cement treated soil was used for the construction of both wedges.

Heave of the surface of embankments, near the abutments, was detected at an early time after the end of the embankments construction during the track leveling monitoring carried out periodically by the railway administration. Afterwards a grid of jet grouting columns was executed on both embankments to stabilize the embankment material. However, heave rate did not stop after the jet grouting treatment. Continuous extensometers installed in boreholes through the embankments showed that strains were developing in the upper 8-10 meters of the embankments (fig. 1).

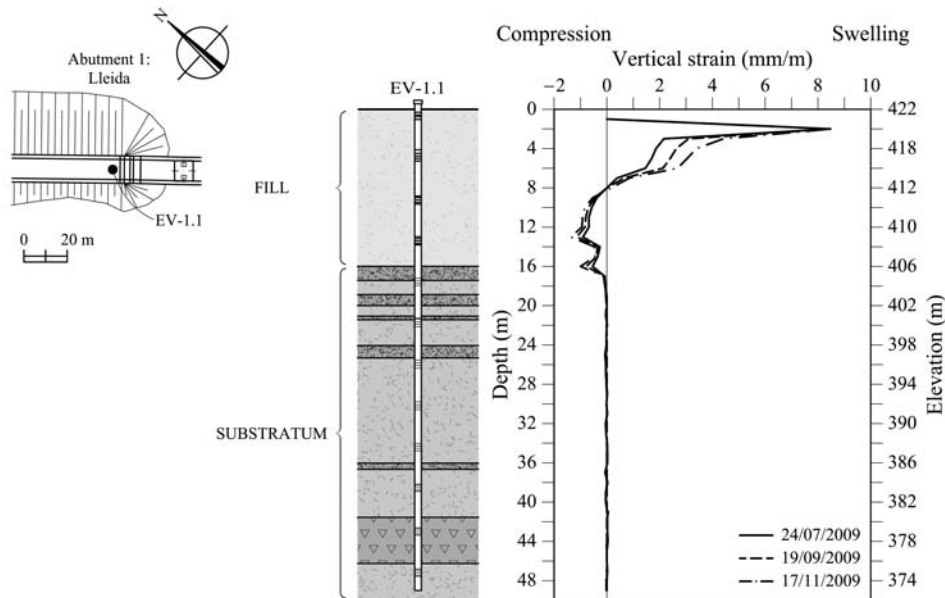


Figure 1: Vertical strains measured by sliding micrometer EV-1.1

Inclinometers installed in boreholes indicated that swelling deformations occur not only in the vertical direction, but also in the horizontal direction. Monitoring of topographic marks installed on the surface of the embankments confirmed that a volumetric swelling was deforming the embankments. The distribution of displacements along the embankment axis agrees with the intensity of the jet-grouting treatment.

Samples of embankment material recovered from boreholes were studied by means of X-ray diffraction (XRD) and scanning electron microscope with an energy dispersive spectrometer (SEM-EDS). Ettringite and thaumasite crystals were found in all the samples analyzed (Fig. 2). Ettringite crystals require an environment with a high pH value and the presence of calcium, sulphates, aluminum and water for its growth. Silicon and carbonates are also needed for the formation of thaumasite. The hydration of cement components, present in the transition wedges and in the jet-grouting treatment, rises the pH value. The

resulting alkaline environment dissolve clay minerals and releases aluminium and silicate ions. High pH values also favor the dissolution of sulphate minerals (gypsum). Then the combination of sulphates from the soil, alumina released from clay minerals, calcium from cement components and gypsum, and the availability of water from rainfall leads to the formation of ettringite. The dissolution of calcite in carbonic acid releases the carbonates which are necessary for the formation of thaumasite from ettringite crystals previously developed. The formation of thaumasite and ettringite is essentially unlimited because of the availability of the necessary components for its formation in the embankments. It was concluded that deformations in the embankments will proceed for a long time if no remedial measures are carried out. A finite element model of embankment swelling was developed to calculate the swelling loads against the bridge abutments and also to estimate the state of stress on the embankments. It was found that a dangerous state of passive stresses had been developed on the upper 8-10 m of the embankment. The costly remedial measures carried out will also be outlined in the presentation.

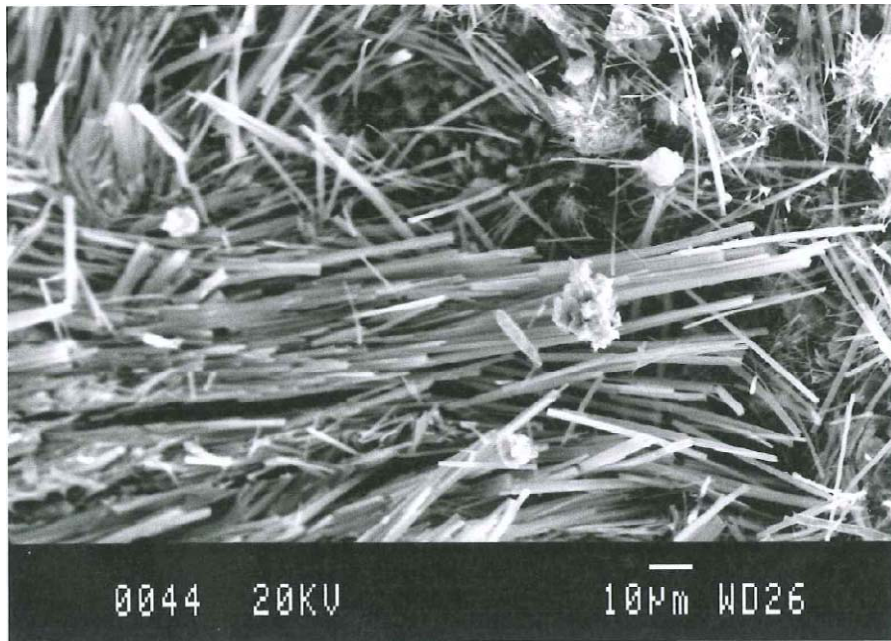


Figure 2: Ettringite needles and thaumasite flat crystals found in a tested sample

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KEYNOTE LECTURE

Pore scale investigation of the mechanisms governing evaporation from porous media

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ABSTRACT

Drying of porous media is strongly influenced by the interplay between transport properties of the medium and external boundary conditions. Initial stages of evaporation are supported by capillary-induced liquid flow connecting a receding drying front (i.e. the interface between saturated and unsaturated zone) to evaporation surface, the so-called stage-1 evaporation. At a certain drying front depth, gravity overcomes capillary and viscous forces and a transition from liquid flow-supported stage-1 to diffusion-supported stage-2 evaporation occurs [1]. Characteristic lengths deduced from transport properties of porous media are proposed to predict the end of stage-1 evaporation under different boundary conditions. Effects of pore size distribution [1], wettability [2-5] and structure [6] of porous media are considered in the proposed characteristic lengths. The model predictions are checked and evaluated by a complete series of micro- and macro-scale evaporation experiments using cutting-edge techniques such as synchrotron x-ray tomography [7] and neutron radiography [8].

Along with the analysis of stage-1 evaporation under different boundary conditions, stage-2 evaporation was investigated in detail. We show that end of stage-1 evaporation is followed by jump of the liquid meniscus from the surface to a level below whose thickness could be estimated by a characteristic length of connected clusters at the secondary drying front (i.e. the interface between unsaturated and dry zone) obeying a power law with the system's Bond number. The subsequent drying is governed by the capillary liquid flow from the wet zone to the secondary drying front, vaporization at that level and vapor diffusion through the overlying dry layer [9].

Besides, new insights regarding dynamics of drying front displacement [4, 8], its three dimensional structure [10] and preferential flows affected by texture, wettability and structural heterogeneity of drying porous media [2, 5-6] are discussed. Our results also offer new tools to manipulate the drying of porous media in desired ways to control the evaporative water losses and also solute transport and deposition patterns in drying porous media [2, 5, 7, 11].

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Magnitude of the stage I drying rate of porous building materials with different porosity

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ABSTRACT

In building conservation, many problems are related to the presence of water in porous materials such as stone, mortars and ceramics. Indeed, moisture can be seen as the catalyst for many deterioration mechanisms. It gives rise to harmful chemical reactions, such as sulphate attack, enables biodeterioration and prompts salt decay, one of the most harmful deterioration mechanisms of porous building materials. A better understanding of drying processes can provide an important basis to find efficient ways of controlling the presence and, therefore, mitigating the damaging effects of moisture. This is particularly important in the case of salt decay because it typically occurs during drying when water and ions are transported towards the surface as the water evaporates. Therefore, a better knowledge of drying is also necessary for the understanding of the decay mechanism itself.

In this study we have looked at the evaporation from various porous materials with different porosity and surface roughness.

Generally, a two-stage model (Fig. 1) is considered appropriate to describe drying of porous materials. The two stages are the constant drying rate period (CDRP), which takes place at the higher moisture contents, and the falling drying rate period (FDRP), at the lower moisture contents. In the CDRP, the drying front is very close to the outer surface. Liquid moisture transport dominates and the evaporation rate is highest. In general, it is in this period that most of the moisture content in a material drying from saturation is eliminated. In this period, if salts are present, they will be transported to the surface where they crystallize as efflorescence.

It is often assumed that the CDRP drying rate is similar to that of a free water surface, due to the presence of a liquid film covering the whole surface of the material during this period. This idea has been contradicted by experimental results of different researchers [1-3], who reported that the CDRP evaporation rate of porous building materials was not necessarily equal, and may even be significantly higher than that from a free water surface subjected to similar environmental conditions.

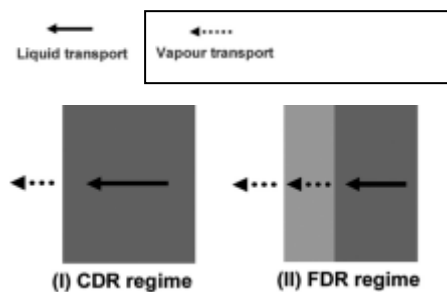


Figure1: Drying of a porous building material

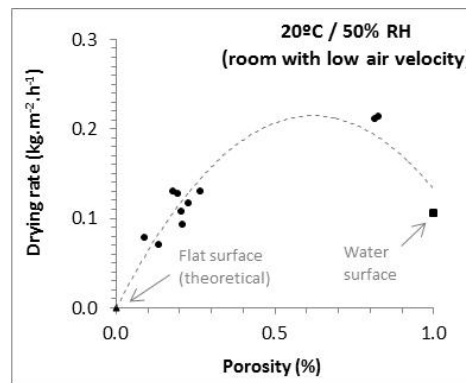


Figure2: Variation of the CDRP evaporation rate with the capillary porosity of the materials

In this study we analyze the CDRP drying rate for eight porous building materials. Both natural stones and artificial materials were tested: the Bentheimer sandstone, four limestone varieties (Ançã, Lecce, Malta's Globigerina, and a Portuguese low porosity limestone), red ceramic brick, slaked lime/sand mortar (1:3 in volume) and three kinds of calcium silicate material. The capillary porosity of the stones, mortar and bricks is in the interval 9-27%, whereas two of the calcium silicate materials (with 82% and 83% porosity, respectively) cover the higher range of values.

Several experiments were performed following RILEM procedure for measurement of the "evaporation curve" [4], at 20°C and various RH.

The results of one of these experiments can be seen in Fig. 2, which shows the CDRP drying rate as a function of capillary porosity. Here, a free water surface is regarded as a material with 100% porosity ($P=1$). Point (0,0) is attributed to a theoretical material with 0% porosity ($P=0$).

These results show that the CDRP drying rate varies among the different materials. In some cases it is lower than that of the free water surface, which is inconsistent with the presence of a liquid film covering the whole surface of the material during this period. In other cases, it is higher than that, as was also found in other studies [1-3].

It can be concluded that the drying rate is a function of the capillary porosity. If we consider only materials with porosity up to 27%, i.e., the common building materials (natural stones, bricks and mortar), the relationship is almost linear, as reported in a previous article [3]. However, when we consider also the materials with higher porosity (above 80%) and the free surface of water (100% porosity), a linear relationship is no longer able to describe this relation. In this case, a better approximation can be made by parabolic function.

We hypothesize that changes in drying rate are due to the variation of the effective surface of evaporation. Roughening with sand or polishing were not successful in creating significant differences in the drying rate of a same material [3]. However, surface texture measurements performed with an optical method revealed that the surface area of the materials increases exponentially as the measurement scale decreases, tending to infinity as the scale approaches zero. This behavior indicates that the measured surfaces have fractal properties, which is in accordance with previous studies. Hence, surface irregularity due to internal features (i.e., porosity) could be relevant to explain the observed differences in the CDRP drying rate. This hypothesis will be discussed based on the obtained results.

Acknowledgements

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Characterisation of sandstone (Kandla Grey) weathering behaviour by frost and salt action

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ABSTRACT

Imported natural building stones are becoming increasingly important in Western Europe, often as a replacement of traditional, locally extracted building materials. Unlike these traditional stones, which have been used for several centuries, the weathering behaviour of newly imported materials in the current climatic conditions is often unknown. Not only are the stones exposed to a lot of water, they also have to be resistant to mechanical stresses created by the crystallisation of de-icing salts in the pore network. These de-icing salts are frequently used in Western European winters, and their use goes together with constant fluctuation between freezing and thawing conditions. De-icing salts can have harmful effects on natural building materials in many ways: by creating a hydration pressure or crystallisation pressure; by having a different thermal expansion than the rock in which they are present; by generating thermal shock (Siegesmund *et al.*, 2002) or by frost salt scaling (Valenza and Scherer, 2006).

Changes in the internal structure of the pore network are difficult to monitor when different weathering mechanisms are active. This means that, in order to understand the influence of de-icing salts, it is of great importance that the materials' inner structure is characterised under changing environmental conditions, with and without the presence of de-icing salts. In this study we focussed on the Indian Kandla Grey sandstone, which is frequently imported in Belgium over the last years. Kandla Grey is a subarkose sandstone, consisting mainly out of quartz and feldspars. The stone contains both macroscopically visible, dark laminations (rutile enriched, figure 1a) and microscopically visible laminations of muscovite (figure 1b).

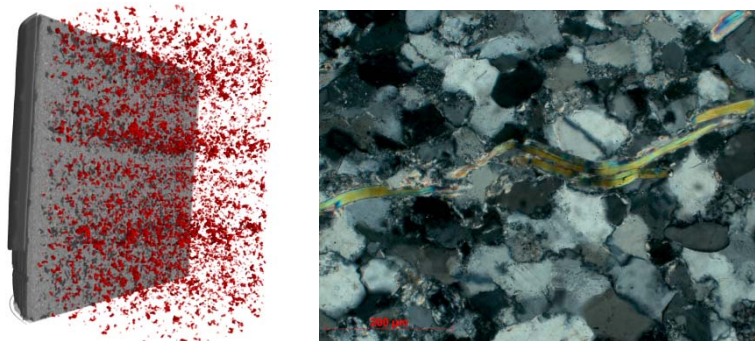


Figure 1: a) Distribution of the dense minerals (rutile) in a 15 mm Kandla Grey core. b) optical microscopy image of Kandla Grey (crossed polars), showing quartz and a mica lamination.

Kandla Grey was first characterised in several ways, according to the European Standards regarding natural stone testing. These tests included capillary water absorption, water absorption under vacuum (to calculate open porosity and apparent density), drying rate and determination of the water vapour permeability. In addition to this, X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to determine the chemical composition of Kandla Grey. Furthermore, the pore structure was investigated using optical fluorescent microscopy, scanning electron microscopy (SEM) and high resolution X-ray

computed tomography (HRXCT, both in laboratory as at the synchrotron facility). The effect on de-icing salts on the thermal expansion coefficient of Kandla Grey was measured using thermo mechanical analysis (TMA). Finally, the weathering behaviour (salt- and frost-induced) was monitored, providing a link between this behaviour and the characteristics of the stone.

Kandla Grey has an open porosity of just 3.02 (\pm 0.62) vol.% and an apparent volumic mass of 2683 (\pm 7.67) kg/m³. Pores are not visible by using traditional optical microscopy, indicating that porosity in Kandla Grey consists almost completely out of micropores (smaller than 1 μ m). SEM demonstrated that the regions around the mica layers are the most porous of the stone. Although water absorption by capillarity showed that the capillary water coefficient C was the same for absorption parallel to the laminations as for absorption perpendicular to the laminations, migration and crystallisation of a saline solution in the material demonstrate that preferential transport along some of the laminations did occur. The total amount of absorbed liquid during the capillarity test is similar when using distilled water or a solution containing 7.5 mass-% de-icing salt solution. When drying the saturated samples of Kandla Grey under constant temperature and relative humidity, the drying rate was lower for those samples saturated with the saline solution compared to those saturated with distilled water. TMA clearly revealed the effects that crystallised salts have on the thermal expansion of a material. When comparing the thermal expansion coefficients of Kandla Grey with and without the presence of salts, values of respectively 12 μ m.m⁻¹.°C⁻¹ and 17 μ m.m⁻¹.°C⁻¹ were found. This indicates that de-icing salts cause additional stresses within the material. When exposing Kandla Grey to the frost resistance test (EN 12371), one out of six samples developed a fracture along its entire length, indicating that Kandla Grey failed to withstand the test. In the European test to determine salt weathering resistance (EN 12370), only spalling of the surfaces of the samples occurred.

Water transport is clearly influenced by the internal structure of Kandla Grey: preferential liquid uptake and water vapour transport occurs along the macroscopically invisible mica laminations. The preferential moisture transport inside these layers causes them to be zones of weakness in the material. Water in these laminations creates a vulnerability towards frost-thaw weathering. Frost weathering phenomena are accelerated by the presence of salts in the pore space, since they cause a drop in the drying rate of the material. Furthermore, these salts have another thermal expansion coefficient than the surrounding material, creating additional stresses due to differential thermal expansion. When using Kandla Grey as a building material for outside use, the intrusion of liquid and saline solutions should be kept to a minimum, since this study demonstrates that the properties of the laminations in the stone influence the frost-weathering behaviour. Based on the experiments that have been carried out in this research, it can be concluded that Kandla Grey has zones that are sensitive to frost and salt weathering in the Western European climate.

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Artificial weathering of lime mortars desalination control by the drilling resistance measurement system

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ABSTRACT

Artificial salt crystallization tests are frequently used as a research tool estimator of the porous materials durability and susceptibility because salt weathering is one of the most important deterioration mechanisms that building materials undergo in a wide range of environments [1, 2]. Pressures created by salt crystallization in pores weaken the material until the overcome of its mechanical strength and material damage [3].

Salt crystallization tests promote artificial deterioration by salt crystallization-dissolution processes that occur in materials interior. For the assessment of deterioration caused by salt crystallization tests, it may be necessary to undertake a desalination process on tested materials.

Desalination may be performed by poultices impregnated with deionized water, or, in the case of low dimension samples, by immersion in deionized water. Desalination evolution may be controlled by monitoring the increasing amount of salts dissolved in the water over time. Since we are in the presence of diluted salt solutions there is a linear dependence between ion concentration and specific conductivity. Therefore, conductivity measurement provides information on the total content of ionic species and, for that reason, on soluble salts. However, this test does not give information about the total amount of salts that remain inside the material and how they are distributed on the sample. The present work shows the possibility of using the drilling resistance measurement system (DRMS) for identifying the salt distribution within the tested samples, monitoring desalination process and assessing mechanical alteration on lime mortars due to salt crystallization.

The drilling resistance test enables the evaluation of resistance in depth and has been used to characterize materials like stones and mortars. Considering that the deteriorated material will not have a higher mechanical resistance than it had before the ageing process, the measurement of higher values of drilling resistance on the aged samples can only be explained by the presence of salt inside the material.

To accomplish the proposed aim, two air lime mortars formulations (CA1 and CA2), with a 1:4 binder-aggregate ratio, by volume, and different water-binder ratio (1.05 and 1.10, respectively), were studied and submitted to artificial salt crystallization ageing tests, employing a sodium chloride solution (15%w/w), after a curing period of 3 months [Figure 1].

The salt crystallization procedure adopted was based on the test performed by Selwitz [4] and Agostinho *et al.* [5] and 3 cycles were performed on standard samples (40x40x160mm), previously dried at 60°C until constant mass. A cycle comprises four phases of a one week period each, the first for the saline solution absorption and the others for the salt displacement and crystallization inside samples. The samples were placed, vertically, inside individual glass dishes with the same amount of saline solution or water according to cycle phase. Paraffin wax was used to prevent evaporation, sealing the system.

Desalination was accomplished by samples immersion, firstly on water supplied by utilities and later on distilled water. The samples of each mortar formulation were desalinated using different containers. Conductivity of the water where the samples were immersed was measured and replaced by the same water volume every week. After a desalination period of 3 months, the conductivity stabilized and the desalination process was ended [Figure 2].

The deterioration of both tested mortars was evaluated by visual observation, determination of mass variation, water absorption by capillarity, porosity, density, ultrasound velocity and drilling resistance.

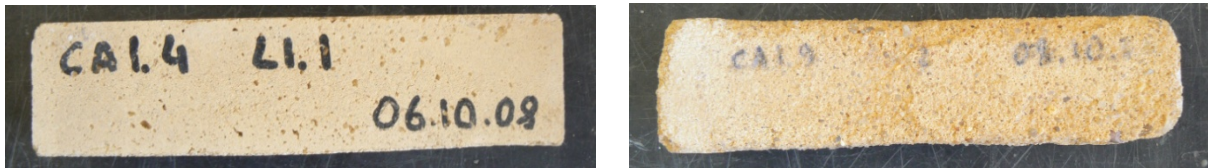


Figure 1: CA1 mortar samples before ageing (left) and after ageing (right).

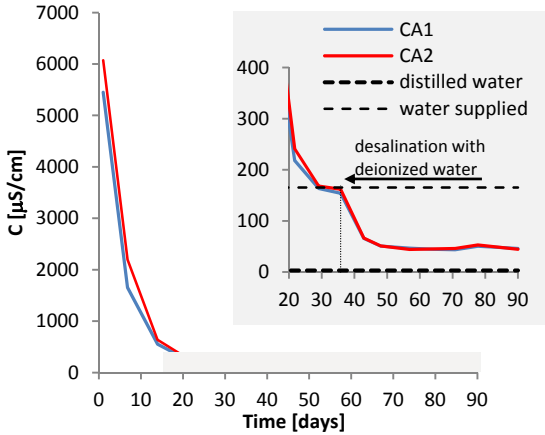


Figure 2: Evolution of the conductivity during desalination.

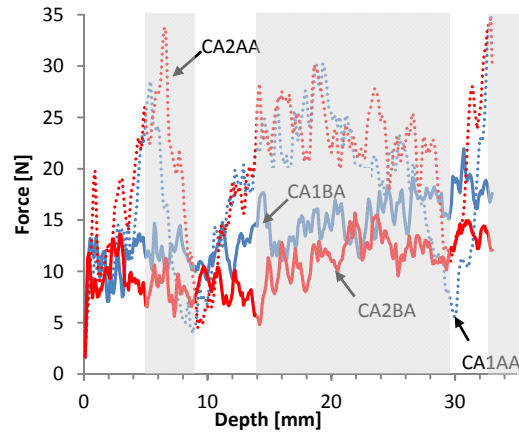


Figure 3: Drilling resistance of the tested mortars before (BA) and after ageing (AA).

After ageing and desalination, both tested mortars registered mass loss [Figure 1] and an increase of water absorption through capillarity. On the contrary, the mechanical characterization performed points to an increment of the mechanical properties of the aged mortars, which can only be explained by the presence of salts inside the tested samples.

The mortars drilling resistance, before and after ageing is presented in Figure 3, and each drilling profile corresponds to an average of 9 drilling tests. The drilling profiles of the tested mortars before ageing show a certain regular drilling resistance in-depth and a higher mechanical resistance for CA1, confirming compressive strength results. The drilling tests performed on weathered samples show an irregular in-depth resistance behavior, which confirms the salt presence inside the samples and gives information about their distribution. Figure 3 enables the identification of salt presence in the following depth ranges: 4-8mm, 13-28mm and >32mm.

As conclusion, the drilling resistance was able to identify salt presence on the desalinated samples and the salt distribution inside the samples, differentiating high resistance results where salts are concentrated and lower resistance results where mortar deterioration was more pronounced. The results point DRMS as a useful tool for monitoring desalination processes, mechanical alteration and salt distribution on lime mortar due to salt crystallization.

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POSTER PRESENTATIONS

Salt degradation in stone of historical Buildings: The importance of water absorption coefficient

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ABSTRACT

The crystallization of soluble salts is a major mechanism of degradation of some building materials, including stone. This mechanism of deterioration is based on the pressure exerted by the formation of salt structures in porous materials, with increased volume and is dependent on the type of salts involved and the size and arrangement of pores. When the pressure exceeds the internal strength of the material, and particularly when the salt formations undergo cycles of crystallization and dissolution in response to fluctuating levels of humidity, the deterioration of materials typically becomes apparent.

It is therefore essential to understand the phenomenon of crystallization and dissolution of salts, i.e., to know the conditions of crystallization of each salt, depending on relative humidity and air temperature.

For this purpose we developed an experimental work, using four samples of stone (one limestone and three granites), which consists, initially, to study the variation of the water absorption coefficient with and without soluble salts (NaCl, $Mg(NO_3)_2 \cdot 6H_2O$ and K_2SO_4). An analyze of the water absorption coefficients values obtained with the classification used with Germany code; it was possible to classify the samples as to their permeability. Thus, the limestone, old granite-1 and old granite-2 samples are classified as “Preventive against water”, while new granite sample is classified as “Water repellent”.

Extraction of sulphates by electromigration in two different granites

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ABSTRACT

Desalination by electromigration is a salt extraction method whose application in cement and concrete (in the case of chlorides) is well developed [1, 2, 3]. In the case of other building materials, there are only references on the application of this method for brick desalination [4]; In the case of other building materials (as ornamental rocks), electromigration as a desalination method has not been addressed sufficiently. The authors of this work have recently applied this method for the first time with the aim of extract the chloride from contaminated granitic rocks [5], obtaining a very satisfactory efficiency. This paper deals with the study of the effectiveness of electromigration in the extraction, also in granites, of sulfate ion; the sulfate salts (gypsum, thenardite and mirabilite) are involved in the development of severe deterioration forms in rocks used in construction (see [6] and [7] and references therein), being responsible, in granites, of the formation of surficial detachments [8].

The method of desalination by electromigration has been applied in two granites from the NW of Iberian Peninsula widely used in construction of the architectural heritage. Both granites, with different texture and pore size distribution, were contaminated with 14% Na₂SO₄ solution.

The desalation effectiveness has been evaluated taking into account 1) the analysis of ion content in anode and cathode during and after the trial and 2) the analysis of ion content in the rock at different distances from the electrodes at the end of the trial. The possible harmful effects on the rock were also evaluated, controlling during the test the pH on the rock surfaces in contact with the electrodes and measuring the color changes on the rocks after the test.

At the end of test, the sulphate content was significantly reduced, indicating that the method is effective even for polyvalent ions such as sulfate. pH changes in anode and cathode that occur during migration have been minimized achieving the maintenance of pH at values near neutrality by means the use of a buffered electrolyte and the placement of poultices with neutralizing capacity between the electrodes and the rock surfaces. The color changes detected after the test seem not to be related to the principle of the method. An influence on the desalation effectiveness of the pore structure of the rocks was also observed, which reaffirms the need of previous characterization and knowledge of the properties of rock materials prior to be undergone a conservation treatment.

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Gypsum efflorescence on clay brick masonry

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ABSTRACT

Efflorescence is a common problem affecting the surface of a building made of brickwork or concrete. It appears mostly as a thin deposit of salts. Most types of efflorescence appear just after construction and are easily cleaned by natural weathering. However, recently in Belgium there is a growing number of complaints about efflorescence appearing on clay facing brickwork after a couple of years of construction (see Figure 1). In contrast to the other kinds of efflorescence, these deposits consist of hardly soluble salts, what makes it very hard to remove. Similar cases of persistent efflorescence, mainly composed of gypsum, were reported in the Netherlands [1] and the UK [2]. There is in general a lack of understanding about the source, the genesis and the mechanism of formation for this type of efflorescence.

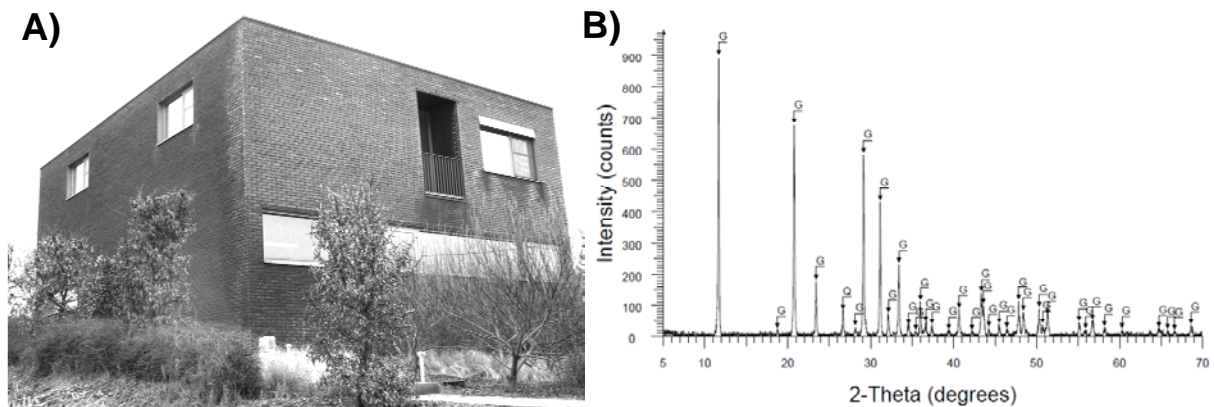


Figure 1 A) An example of a house affected with persistent efflorescence. B) An XRD analysis of the deposit collected from the house showing clearly that efflorescence is composed of gypsum (G).

A specific source of soluble sulphates is necessary for the development of gypsum efflorescence. This kind of efflorescence occurs typically after a couple of years, suggesting that the availability of this sulphate source is delayed by some processes that progress after the wall construction.

Although sulphates may originate from many sources as for example mortar, brick, rain and soil, it seems that in case of the gypsum efflorescence the source of sulphates is mortar. The origin of sulphates in mortars could be the addition of gypsum to control the setting of cement. During the hydration of cement, sulphates are recrystallised into ettringite and monosulphate phases. A hypothesis was proposed indicating the source of gypsum may be the carbonation of cementitious phases, which were developed during mortar setting [1]. Several published papers reported that ettringite decomposes due to carbonation to i.e. gypsum and vaterite [3–5].

The aim of this project is to reveal the mechanism of the development of the persistent efflorescence and to use this expertise in order to design a mortar with a low GL-efflorescence risk. During a field survey, the first part of this research, we investigated a number of buildings showing persistent efflorescence. The aim of this first step is to identify salts forming the deposit, characterize the appearance of efflorescence and gather relevant data such as the type of brick type used for construction and the age of a building. These data are put into a database, which is later analysed to determine which salts form persistent efflorescence, factors which hinder or facilitate efflorescence development and to choose materials for further studies.

In the next step we will collect samples of bricks and mortars from selected locations. These samples will be analyzed to identify minerals which may be a potential source of efflorescence. Their distribution may already give an indication of the mechanism of efflorescence development. If the case study confirms that the carbonation of mortar may trigger the soluble sulphates source, we will investigate this mechanism in laboratory conditions. It will be realised by subjecting cement paste samples to accelerated carbonation conditions and monitoring the development of soluble sulphates and mineral composition. The knowledge

of the mechanism will be the basis for designing an accelerated test method to develop persistent efflorescence on masonry wallettes. This method will be applied to study the impact of brick properties and to design a mortar formulation with no or low risk of persistent efflorescence.

The samples of deposits were collected by gentle scraping the surface affected with efflorescence. The mineralogical composition of the collected samples was determined by powder X-ray diffraction with a Philips PW1830 diffractometer using CuK α radiation (45kV, 30mA). Standard 2 θ scan range was taken as 5-70° with a step size of 0.02° 2 θ and a counting time of 1s.

During the field survey we have analyzed 19 cases of persistent efflorescence, for 10 of these buildings the age of construction was known and varying between 1997 – 2010. All the investigated houses were made with hand-moulded bricks. The deposit may have different forms: varying from foggy efflorescence, where single grains of salts forming deposit may be distinguished, to a thicker layer of deposit tightly covering the surface of masonry or even locally occurring crust. In most cases efflorescence affects the brick to a greater extent than the mortar. Nevertheless it is evident that efflorescence develops on mortar as well, but usually a slight or moderate discoloration is apparent. In all cases the most affected facades of a building are these facing west, south and south-west direction. This may be explained by the fact that walls facing these directions are the most exposed to the action of rain and wind. The efflorescence is pronounced on upper parts of the façade and on the edges of a building facing south, west or south-west direction. The appearance of efflorescence changes over time, it may depend on the age of the building, time of the year and the dampness of masonry. Nevertheless, it doesn't wash with natural weathering, it permanently affects the appearance of a building.

The XRD analysis revealed that in most cases efflorescence is composed of gypsum. In some cases no gypsum was identified and besides quartz only low amounts of calcite were identified. When gypsum was identified in the sample it was evident that it originates from the efflorescence. In case of calcite its origin in the collected sample scraped from the surface of a brick cannot be unambiguously determined. Calcite is used as a component of sanding mix for some types of bricks, it may be naturally present or added to clay and may develop on the surface as efflorescence. For 3 cases showing gypsum efflorescence we identified brick types and acquired their relevant characteristics. These bricks are characterized by very low soluble sulphates content (below 0.02 %), thus it is unlikely that they are the source of the component of gypsum efflorescence.

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Crystallization behavior of $\text{NaNO}_3\text{--Na}_2\text{SO}_4$ salt mixtures in sandstone and comparison to single salt behavior

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ABSTRACT

Crystals growing in confined spaces can generate stress and are a major cause of damage in porous materials. While the behavior of several single salts commonly found in building materials is well characterized, only few studies have been carried out on the behavior of salt mixtures. Besides the single salts formed by all possible binary cation–anion combinations, a number of double salts can crystallize from salt mixtures. Not much is known about crystallization behavior and damage potential of double salts. This contribution presents results of an experimental study with the double salt darapskite ($\text{Na}_3\text{NO}_3\text{SO}_4\cdot\text{H}_2\text{O}$) which is an incongruently soluble double salt. Such salts show a complex crystallization behavior and may have a great damage potential, because a solution supersaturated with one of the single salt compounds is formed during the dissolution of the double salt. Therefore, crystallization and damage may occur at high relative humidity or during wetting. Experiments were carried out with sandstone samples ($15 \times 15 \times 20 \text{ mm}^3$) with sealed surfaces on four sides. The samples were impregnated with mixed $\text{NaNO}_3\text{--Na}_2\text{SO}_4$ solutions. For comparison, samples were also treated with three single salts (NaNO_3 , Na_2SO_4 , MgSO_4). After treatment with the salt solutions the samples were exposed to wetting/drying cycles. Damage occurred already after few cycles and was detected by visual inspection, weight changes of the samples and by optical microscopy. It is confirmed that those salts that form supersaturated solutions during wetting of the samples, i.e. sodium sulfate, magnesium sulfate and darapskite have a higher damage potential than sodium nitrate. The phase changes during the wetting–drying cycles were studied by Raman microscopy and are compared to the phase diagrams of the respective salts.

Capillary suction and drying of natural hydraulic lime and of air lime based mortars

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ABSTRACT

Air lime and natural hydraulic lime are different binders for mortars to be applied on ancient construction protection. The type of lime, the use of pozzolans, as metakaolin, and the influence of curing conditions are studied in order to evaluate mortar capillary water absorption and drying, when compared to other mortar characteristics.

Introduction

Lime-based mortars were widely used in the past namely as masonry mortars, rendering or plastering mortars. Until the XIX century mortars were based on air lime (calcium hydroxide). Sometimes pozzolans were added to air lime mortars in order to obtain hydraulic behaviour. In fact, in some applications with low contact with carbon dioxide or abundant contact with water, hydraulic behaviour was needed; otherwise air lime mortars would be unable or would take too long to carbonate. Only by the XIX century natural hydraulic limes appeared. These types of limes, made with calcium carbonate rock but with some amount of clay, still had calcium hydroxide but mainly hydrated compounds.

Many ancient buildings and other structures, as the case of masonry bridges, are still in use worldwide. They are made of lime mortars, with or without pozzolans. Many of those constructions need urgent repair, with mortars that assure their protection [1].

In order to achieve knowledge to lime-based mortars characteristics, pure air lime and recently classified natural hydraulic lime mortars or mortars with these types of lime with different amounts of metakaolin were exposed to different curing conditions characterized and presented in this work.

Experimental

Mortars were fabricated with binder:sand volumetric proportion of 1:3. The binders were a CL90 air lime LUSICAL H100, a NHL3,5 natural hydraulic lime SECIL and a NHL5 natural hydraulic lime SECIL. These two last binders are new products, recently formulated and classified by the recent version of EN 459-1:2010 [2]. The pozzolan was a metakaolin Argical M 1200 S from IMERYS (Mk). When metakaolin was used, the weight percentage of lime was replaced by the same weight of metakaolin. The percentage of lime substitution by metakaolin in the formulated mortars tried to be related with the hydroxide calcium available in the lime. The sand was a mixture of three calibrated washed siliceous sands (Table I). The mixture of the three sands was previously optimized to achieve a good grading curve.

After demoulding, mortar samples were exposed to laboratorial humid (90% RH) and standard (65% RH) curing and to natural maritime exposure (at Cabo Raso LNEC station).

Mortar samples have been tested at the age of 28 days (and some have been presented elsewhere [3]) and are currently being tested at 90 days for mechanical resistance (dynamic modulus of elasticity, flexural and compressive resistance, resistance to sulphate attack) and for physical characteristic (open porosity, water capillary absorption and drying). These last characteristics will be particularly analyzed in this work.

At 28 days, among other situations:

- the curing conditions were more important for NHL5 and for air lime mortars than for NHL3.5 mortars, and the variation was lower for physical characteristics;
- the substitution of lime for metakaolin improves the capillary coefficient of hydraulic lime mortars and worsen the one of air lime mortars; generally it had no influence on asymptotic value of capillary absorption;
- mortars with NHL3.5 present drying conditions comparable to air lime mortars but the lime substitution for metakaolin slightly difficult the drying of NHL3.5 in all curing conditions.

At the 90 days of age results are still under analysis and will be presented in the conference.

Mortar	Volumetric prop.	Weight Proportion	W/B	Consist. [mm]
CL	1:3	1:12	2,5	158
CL_30Mk	1:3	1:12	2,5	154
CL_50Mk	1:3	1:12	2,6	154
NHL3.5	1:3	1:5	1,1	153
NHL3.5_10Mk	1:3	1:5	1,1	149
NHL3.5_20Mk	1:3	1:5	1,1	143
NHL5	1:3	1:5	1,1	161
NHL5_5Mk	1:3	1:5	1,1	156
NHL5_10Mk	1:3	1:5	1,1	149

Table 1: Designation (type of lime and w% lime substitution for metakaolin), volumetric and weight proportions, water binder ratio and mortar flow table consistency

Conclusions

Comparison can be made showing the influence of the type of lime, the presence of the metakaolin partially substituting the lime and the curing conditions. Characteristics are compared to the expected evolution with ageing [4] and to bibliographic range values [5] that point out the adequacy of the different mortars to different types of application on the repair of ancient buildings and structures, as repointing and rendering mortars. The importance of these parameters on mortar characteristics is highlighted.

Acknowledgments

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Capillary water absorption of unstabilized and stabilized earth materials: anomalous time scaling behaviour

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ABSTRACT

Building materials based on natural earth bear important environmental advantages and, so, are becoming widely used all over the world. However, their behaviour as construction materials for walls (rammed earth, adobe) or in mortars (plasters and renders, repair or bedding mortars) is still poorly understood and usually addressed at a purely technological level.

To improve their mechanical resistance and reduce clay swelling, earth-based materials are often stabilized with small amounts of lime or cement.

Here, we present a set of one-directional capillary water absorption experiments [1] performed with four types of earth. Indeed, water is involved in most decay processes and, as evidenced by practice, can be particularly harmful for earth-based materials. To understand the hydric behaviour is, therefore, essential for this type of material.

One of the earth materials is a commercial earth. The other three were collected from the walls of unstabilized rammed earth buildings located in Alentejo region, in south Portugal. The four materials are fully characterized elsewhere [2, 3]. The commercial earth was tested after stabilization with dry hydrated air lime, natural hydraulic lime, Portland cement or natural cement, as well as unstabilized.

The results showed that the unstabilized materials have anomalous capillary suction behavior, evidenced by nonlinear (exponential) $t^{1/2}$ dependence during the first minutes. The irregularity is especially significant for the commercial earth, but disappears with the addition of even the smallest amounts of binder (5% weight).

The anomaly is probably due to the volume increase of the clay particles as they contact with water, reducing the pore size and, thus, increasing the amount of capillary pores. The use of stabilizers eliminates clay swelling, thereby enabling linear $t^{1/2}$ dependence in the capillary suction tests.

Despite the regularization of the suction behavior, the stabilizers can hardly be considered to have improved the hydric performance of the earth materials. In fact, they increased the capillary suction and the maximum amount of water absorbed, i.e., the capillary porosity of the material. These effects were more relevant for the air lime and, above all, for Portland cement, but they were also obvious for the higher contents of hydraulic lime and of natural cement. Alike results were obtained for the case of cement stabilization in a previous study [4]. The present results show that other hydraulic binders and also air lime can have similar effect, suggesting that all of them can significantly increase the quantity of capillary pore space in the earth material.

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Influence of ferrocyanide ions on NaCl crystallization in the mixture of salts

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ABSTRACT

While the mechanisms of salt damage in porous materials have received considerable attention in recent years, effective treatment methods for ameliorating this common problem still remain limited. Recently, the use of ferrocyanide inhibitors has been proposed as a potential preventive treatment method against NaCl damage [1]. Although NaCl is one of the most widely distributed salt, in practice NaCl is accompanied by the presence of other salts in the building materials. The presence of salt mixtures presents a totally different behavior. Thus, before using the inhibitors in practice a better understanding of the kinetics of salt crystallization process in their presence is required. This behavior is still not completely understood, because it is not easy to measure the concentration of ions during dynamic measurements. However, with the help of a specially designed Nuclear Magnetic Resonance set-up [2], we were able to measure both hydrogen and sodium ions simultaneously during dynamic experiments and can thus provide information about the salt concentration. A series of micro-droplet drying experiments were performed with NaCl and mixture of NaCl and KCl solution with and without crystallization inhibitor inside NMR. The main focus was on the effect of the potassium hexa-cyanoferrate (II) tri-hydrate $K_4 [Fe (CN)_6] 3H_2O$ as an inhibitor on the crystallization of NaCl in the presence of other salt. The NMR measurements are coupled with time-lapse microscopy. This gives the possibility to visualize the drying of the droplet while simultaneously obtaining information about NaCl concentration in the droplets. The information of the crystal size and the crystal growth was gathered from the images captured using time lapse microscopy. Such a powerful experimental set-up helps to attain all the information regarding the concentration of the ions and kinetics of NaCl crystallization together.

The results show, for NaCl solution in the presence of inhibitor a delay in crystallization and higher supersaturation was seen prior to the onset of crystallization. However, no significant supersaturation was seen for NaCl in the presence of KCl. Although in both the cases a significant decrease in crystal size and change in crystal morphology is observed. The crystals formed in the presence of inhibitor were more like a fluffy powder and were not strongly adhered to the substrate. Such type of crystal morphology helps to crystallize salt as non-destructive efflorescence. Thus, the use of ferrocyanide as an inhibitor may provide possible solution to the damage problem.

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