Preface

The longevity of many historic monuments and sculptures, buildings as well as of civil engineering structures is threatened by diverse weathering processes, prominent among which is the internal stress exerted by salts and ice crystallizing in the pores of the material. As an example, this picture shows the advanced state of deterioration of a beautiful chapel in Yorkshire (UK), the Howden Minster in UK, which is suffering the damaging action of magnesium sulphate salts.



Salt weathering of stone (and of other construction materials and rocks) and frost damage results from the combined action of salt transport through the porous network and the in-pore crystallization under changing environmental conditions. The crystallization pressure exerted by the crystals on the pore surface is the main agent responsible for damage. New experimental methods are contributing to a better understanding of the phenomena involved in salt weathering and frost damage. **Increasing** computational power permits numerical simulation of salt weathering processes from the molecular to the macroscopic scale. Indeed, continuum and discrete models are being developed to answer many remaining questions, particularly

including the interaction between multiple and multi-scale phenomena.

CrysPom focuses on fundamental understanding of crystallization in porous materials and the resulting damage mechanism. Thermodynamics and kinetics of crystal growth, material damage by crystallization and failure, salt mixtures, experimental techniques to study crystallization and models such as poromechanics or pore-level models are some of the topics that are presented in CRYSPOM II. By understanding better the chemomechanics of in-pore salt crystallization, more reliable protection of our buildings against salt weathering will become possible.

We aim to bring together leading researchers and Ph.D. students to provide for a constructive and open dialogue and to incite collaborations between theorists and experimentalists at an international level.

Keynote speakers

Crystallization dynamics and salt weathering of stones

N. Shahidzadeh-Bonn.

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Salt contaminated porous materials (such as stones or masonry materials) are often observed to deteriorate under environmental conditions due to crystallization of the salts. These can be naturally present in the stones, or get trapped inside the porous material for instance by imbibition with salt-containing precipitation. When environmental conditions such as humidity or exposure to rain or rising damp vary, salts in contact with water (liquid or vapor) can dissolve and cause damage to the material by re-crystallization upon drying.

I will present experiments assessing the impact of such re-crystallization dynamics of sodium chloride and sodium sulfate on damage observed after repeated cycles of wetting/drying and humidification/drying. Combined macroscopic and microscopic-scale experiments show how the kinetics of crystallization can be related to damage for the sulfate when rewetting is done with liquid water. The former leads to severe damage because of the only partial dissolution of anhydrous microcrystals in regions that are highly concentrated in salt. The remaining microcrystals act as seeds to form large amount of hydrated crystals creating grape-like structures that expand rapidly. We show that the growth velocity of the hydrated crystals in the form of clusters is more than an order of magnitude faster than for hydrated crystals that grow independently in the solution, giving rise to a crystallization pressure higher than the tensile strength of our sandstone. On the other hand, if sulfate-containing stones are slowly rewetted by bringing them in contact with saturated water vapor prior to drying, hardly any damage is observed. These differences will be discussed.

Articles related to this work:

Shahidzadeh- Bonn et al , Langmuir 2008.

Shahidzadeh-Bonn et al, Poro Mechancis IV, 4th Biot Conference proceeding, 2009.

Shahidzadeh-Bonn et al, Phys Rev E, in press 2010.

Impingement of crystals during precipitation in pores

George W. Scherer ¹, Rosa M. Espinosa-Marzal ²

When crystals of salt precipitate in stone, their growth is inhibited by collisions with each other and with the pore walls. The standard Johnson-Mehl-Avrami-Kolmogorov model assumes that nucleation takes place at random sites throughout the volume and impingement is incorporated in terms of excluded volume (i.e., crystals cannot nucleate or grow in regions already crystallized). Johnson and Mehl introduced a variation on this model to describe phase changes in metals, in which nucleation occurs on grain boundaries and growth is contained within the grain. To describe growth of crystals in a porous host, it is reasonable to assume that nucleation occurs on the pore walls and that growth is contained within the pores, which is similar to the Johnson & Mehl model. Unfortunately, they considered only spherical "pores" and the details of their analysis were not published. Recently, Villa and Rios presented analyses of growth in confined spaces of various shapes where nucleation occurs at a constant rate or from a fixed number of sites. We have applied these models to simulate growth in pores to see under what circumstances the impingement conditions have a strong effect on the shape of the curve. By fitting data for crystallization of sodium sulfate in limestone, the performance of the models is evaluated, and the apparent rates of nucleation and growth are compared.

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Salt crystallization in porous media: new strategies for conservation of stone affected by salt weathering

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Salt weathering is recognized as a hazard endangering the built and sculptural heritage. Although much research has been dedicated to understand salt weathering of porous building materials, there are several important aspects of this decay process that remain unknown. This lack of knowledge has prevented the development of effective conservation methods to halt or mitigate salt weathering. Here we show that salt weathering results from the combination of chemical (salt-enhanced dissolution) and physical (crystallization pressure) weathering processes. Regarding the physical weathering associated to salts, the critical supersaturation of different saline solutions undergoing evaporation from a porous material (glass frits), and the resulting crystallization pressure reached when salts crystallize within the pores have been studied by combination of in situ 2D-XRD (using highly penetrative Mo K α radiation) and DSC. This approach also enables the identification of the phase that creates damage (i.e., crystallizes first) and the crystallization sequence (e.g., Na₂SO₄·7H₂O □ Na₂SO₄·10H₂O □ Na₂SO₄). Chemical weathering associated to salt solutions has been studied by in situ AFM. This technique yields accurate (nanoscale) information on the dynamics and kinetics of salt-enhanced substrate dissolution. Based on these results a new approach to halt both chemical and physical damage of porous materials associated to soluble salts has been developed. It includes the bacterial biotreatment of stone and the development of protecting biofilms. Such biofilms drastically reduce the dissolution rate of the substrate and may enable the crystallization of salts at a very low supersaturation (i.e., low crystallization pressure) by enhancing heterogeneous nucleation of the salt on the biofilms.

The formation of meta-stable sodium sulphate heptahydrate in porous materials as studied by NMR

L. Pel

Transport in Permeable Media, Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands.

Salt weathering is a major cause of deterioration of porous building materials. Of the salts responsible, especially sodium sulfate is seen as very damaging. However many questions have emerged in recent years concerning which sodium sulfate phase will crystallize out during salt weathering and hence what the real damage mechanism is for the damage seen in situ.

In this study we focused on the crystallization of sodium sulfate both in bulk and in porous materials saturated with a sodium sulfate solution. Hence building up a picture of the influence of a porous material on the crystallization behavior of sodium sulfate. The crystallization was induced either by cooling down the sample or drying the sample. As a major tool for studying the crystallization we have used Nuclear Magnetic Resonance (NMR). Using this technique we can measure non-destructively the moisture and ion concentration in the solution during the crystallization and get a direct indication on the phase which is crystallizing out. For bulk solution measurements the NMR was combined with a digital microscope giving the possibility to relate the concentration directly to the observed crystals. These experiments have been performed for various concentrations and building materials. In almost all experiments i.e., over 95%, we observed the formation of a metastable phase of sodium sulfate: the heptahydrate (Na2SO4.7H2O). These observations have been confirmed by DSC and XRD measurements. Only under extreme conditions we have seen the transformation into mirabilite. Hence it seems that the nucleation of heptahydrate is relevant for understanding crystallization in porous material and damage mechanism of sodium sulfate.

Mechanisms involved in efflorescence localization at the surface of a porous medium due to wick action

M. Prat^{1,2}

We consider the classic situation where one face of a porous material is in contact with porous salt solution and the opposite face is exposed to air with less than 100% relative humidity. Wick action draws the salt solution into the material and evaporation occurs at the surface of the porous medium. Observation of crystallization under these circumstances generally shows that efflorescence appears in particular points of porous medium surface. From a series of experiments and some numerical simulations, we propose an explanation to this discrete occurrence phenomenon and identify the main mechanisms controlling the localization of the crystallisation spots.

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Salt mixtures in building materials: Stable and metastable crystallization pathways

M. Steiger

Department of Chemistry, University of Hamburg

A brief review of the composition of salt mixtures typically found in building materials is provided and models to predict the crystallization pathways of salt mixtures are discussed. Such models are very useful tools to predict the environmental conditions that help to minimize the damaging effects of salts in building materials, i.e. the conditions that reduce the frequency of phase changes inducing crystal growth. However, these models are equilibrium models, thus, the formation of stable phase assemblies is assumed. In contrast, metastable crystallization pathways are now well characterized for several salts that are commonly found in building materials, e.g. Na₂SO₄ and MgSO₄. The ability of equilibrium models to predict both stable and metastable crystallization pathways is discussed in detail.

Premelting, pattern formation and the phase behavior of colloidal suspensions

J. S. Wettlaufer.

Yale University, USA.

When the free surfaces of most solids, such as ice, approach their bulk melting temperatures from below, the molecular structure of the material gives way to a disordered structure with some attributes of both the solid and liquid phases. When the temperature is sufficiently close to that of bulk transition, the surface melts and literally flows as a viscous fluid. This phenomenon, called interfacial premelting, lies at the heart of the microscopic theory of melting of solid matter. The process is ubiquitous and responsible for a wide range of consequences in materials with biological, geophysical, and technological significance. When a colloidal suspension such as a soil or a building material is frozen, there remains a distribution of unfrozen—premelted—water to rather low temperatures, the quantitative understanding of which requires a fundamental treatment. The fluid pressures associated with the intermolecular forces responsible for premelting are enormous, driving fluid motions that, among other things, have deleterious effects on engineered structures whilst creating a range of compelling and interesting patterns in a variety of natural settings. Moreover, one discovers the potential to control the distribution of particles in a matrix by the exploitation of Onsager reciprocity. In this talk I focus on these and other consequences of the premelting of solids as they play out in simple and complex geometries.

Crystallization pressure in stone and concrete

R. J. Flatt¹, G. W. Scherer².

Stone and concrete share a number of common points, being porous inorganic construction materials that when exposed to specific conditions can degrade due to similar mechanisms, including crystallization pressure.

There are, however, a number of key differences between these materials. Stones, for example, have pore sizes that are much larger than concrete, and an internal specific surface that is much smaller. In most cases, salt crystals that exert damaging stresses in concrete result from a reaction between a sulfate source and calcium aluminate phases that are components of the cementitious binder. All these differences greatly impact the extent to which these materials may degrade under given conditions.

This paper will discuss this issue briefly and then focus on some cases where the greatest number of analogies can be found. This concerns the crystallization of mirabilite in stone due to wetting or temperature changes, and that of ettringite in the process of delayed ettringite formation. In both cases, arguments are developed about how to evaluate conditions of supersaturation to evaluate stresses.

Emphasis will then be put on delayed ettringite formation, for which the thermo-mechanics of damage are examined. Stresses at the pore scale are calculated and with the amount of ettringite forming, an average hydrostatic tensile stress in the solid is calculated and compared to the tensile strength of tested samples.

Results indicate that, when the loading rate dependence of tensile strength is taken into account, it is possible to rationalize factors that do or do not contribute to damage, such as ettringite content, temperature and fly ash content. Although a number of important assumptions are made and clearly indicated in the paper, the results do open a new perspective onto durability studies that goes beyond the sole case of delayed ettringite formation. Finally, implications for the case of stone are also discussed.

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Conservation treatments for salt-laden stone in Egypt and Adelaide

E. Doehne¹, E. Johnson², P. Lopez-Arce³

The installation of the Aswan dam in Egypt and the removal of billions of native trees in Australia have had similar environmental consequences, such as extensive irrigation, rising water tables, and the salinization of soils. The process of salinization has resulted in over 400 buildings in the City of Adelaide, Australia being treated for salt damage and stone monuments in Egypt, such as the ancient temples of Luxor and Karnak, being threatened by salt damage.

Given the importance of these temples, large-scale engineering efforts have been undertaken in Egypt to locally lower the water table below the temples using a buried perforated pipe and a pump to remove the water to the Nile. This "dewatering" approach has left some remnant soluble salts that are being removed with a local clay/sand poultice. As part of a training course for Egyptian conservators, the poultice was tested to determine the appropriate conditions for its use. The results showed that slow drying conditions for the clay/sand poultice removed about twice as much salt as fast drying conditions (due to less problems with pultice detachment). The clay/sand poultice performed significantly better than the cellulose poultice, which tended to to push the salts deeper into the brick.

Damp proof course failures in Adelaide result in rapid damage to stone, brick and plaster. Treatments have focused on restoring an effective damp proof course. Foundation damage below the damp proof course is notable in some Adelaide buildings when the layer is found more than 20-30 cm above the ground level.

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Talks and Posters

A continuum model of inclusions growing in finely dispersed micro-cracks

A. Alaoui¹, M. Bongué Boma².

Sulfoaluminate clinker is a promising substitute to the most widely used Portland clinker, enabling to lower by 40% the emission of CO_2 per tone of clinker and leading to the production of low shrinkage, rapid hardening and high strength concrete. The main hydration product is ettringite shown to be responsible for the early damage of numerous Portland concrete structures. It is therefore crucial to assess and then prevent damage that may result from delayed ettringite formation (DEF) in sulfoaluminate concretes.

Cement paste constitutes a porous network allowing the transport of water and reactants needed for the formation of ettringite. The latter crystallizes in the free spaces of the matrix and creates stresses on the paste as soon as the voids are completely filled; those stresses may promote expansion and may privilege further damage. DEF is consequently favored by small pores and micro-cracks within the cement paste.

We propose to use the mechanical model of micro-cracked bodies proposed by Bongué Boma *et al.*, to model the damage due to the delayed crystallization of ettringite. Each material element is assumed to be a domain of finite size comprising one single crack. We assumed that each crack is fully entrained by the macroscopic movement. The description of the evolution of the body is split into two ideal steps:

- (i) propagation of micro-cracks;
- (ii) deformation with non propagating micro-cracks.

Given then the chemical kinetics of crystallization, we are able to calculate both global deformation and micro-cracks propagation.

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Salt crystallization induced by evaporation in porous media

M. Angeli¹, D. K. Dysthe¹, C. Raufaste²

Evaporation is one of the two processes (with temperature variations) that can cause salt crystal nucleation and growth from a brine. The objective of this study is to observe directly this process through artificial porous media in order to obtain information on the kinetics of the process. This information could be critical for the understanding of the general process of rock damage caused by these salt crystallizations.

Several types of artificial porous media have been used to observe the nucleation of salt crystals during evaporation in room conditions. Several pore sizes, geometries and salts have been tested in order to find general patterns that could explain different damage potentials or crystallization patterns depending on the type of salt and the type of rock. Results show that some salt have a tendency to enhance evaporation while other inhibit it; some salts tend to precipitate within the porous medium and some other precipitate at the edges; some salts tend to be all precipitating in the same location while others are more homogeneously distributed within the medium.

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Mass transport in the material boundary layer during drying: experiments with sixteen paint coatings applied on dry or wet lime mortar substrate.

V. Brito¹, T.D. Gonçalves¹, P. Faria²

While accessing the drying behaviour of sixteen (water borne) paint coatings applied on air lime mortar substrate, we found a surprisingly good (linear) correlation between the drying index (DI) and vapour permeability (expressed by the equivalent air layer thickness - Sd). We did not expect to find such a good correlation because drying involves not only vapour but also liquid transport. This result indicates that the liquid transport properties of coatings may have little or no effect on drying. Indeed, the capillary suction of the sixteen coatings is not equal and the results concern also uncoated mortar specimens. One major hypothesis is that the material boundary layer can remain dry even when the evaporation front is located at the surface.

We carried out similar experiments where the same coatings were applied and cured on a permanently damp substrate. In this case, the DI-Sd correlation is much weaker. This indicates that data obtained for coatings applied on a dry substrate may well not represent the behaviour of coatings applied on a wet substrate, which often happens in reality in the case of damp salt loaded walls.

These conclusions have implications in the study of moisture transport and decay mechanisms of porous building materials, namely salt decay (to which the depth of the evaporation front is a key-issue).

We will address the framework of the research, describe the methods and materials used, as well as present in detail and discuss the experimental results.

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Cooler for studying freezing and melting of water in porous geomaterials by NMR

D. Bytchenkoff

U. R. Navier (LCPC-ENPC-CNRS)

We intend to study mechanical effects of freezing and thawing on bulky samples of concrete by nuclear magnetic resonance. To do so, we designed and built a cooler that can be inserted into the probe of an NMR spectrometer to bring the temperature of a bulky cylindrical sample to -100°C. The cooler is intended first and foremost for experiments in which the NMR signal of water hydrogen will be registered. Therefore, the part of the device that will be placed in the active zone of the NMR probe is made of non-magnetic non conductive materials containing no hydrogen isotope to avoid that it emits any extra signal that could interfere with that emanating from water protons of the sample. Furthermore, a cryostat, pump, air compressor and several other auxiliary components of the device were all put outside the Faraday cage built around the NMR spectrometer to minimise noise that they can induce in the NMR probe. Optical fiber sensors were built into the cell to provide for monitoring temperature and mechanical deformations by the means other than NMR. The cooler was designed to use a commercial coolant'Galden' for heat transfer and has advantage of maintaining the radiofrequency field emitter/receiver coil of the spectrometer at room temperature.

Hygric dilation of containing clay sandstones contaminated by salts

E.A. Colas ^{1,2}, J.D. Mertz¹, C. Schneider², V. Barbin²

Strasbourg Cathedral was originally built in Triassic Meules sandstones and restored with Meules and Vosgien sandstones. These rocks are composed of quartz (≈70-90%), K-feldspar and micas in a clay-coating matrix associated with iron oxi/hydroxide. Due to limited volume of exploitable rock materials, constant prospecting of new compatible and durable sandstone for restoration works is needed.

Durability of stones is related to stone properties as well as local climatic conditions on buildings. One of the main weathering factors on building stones is crystallization of salts inducing stone weakening by repeated cycles of dissolution/crystallization. Dilation has been highlighted as a relevant way of studying salt crystallization in materials structure.

A comparative study by determination of mineralogical and structural parameters on 5 sandstones from guarries and 2 sandstones from Strasbourg cathedral was carried out.

Hygric dilation was performed under isothermal conditions by means of relative humidity cycles varying from 15 to 90%. Hygric dilation of salt contaminated sandstones with NaCl and Na2SO4 were measured. Concentrations of salt solutions, 45 g/L and 180 g/L, were respectively chosen to reach an average weight increase of 0.2% and 1% of sandstones.

Hygric dilation of sandstones was well correlated to clay coating properties, amount and specific surface area, showing that intracrystalline swelling of clays had a relevant impact on stone deformation.

After salt contamination while remaining reversible, dilation of stones, i.e. amount and curves shapes was modified, hence stones can be distinguished. NaCl had a greater impact on stone deformation than Na2SO4, intensified by the increase of salt content.

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Performance of limestones loaded with a Na2SO4-NaNO3 mixture

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A research was done in order to examine the behaviour of two types of limestones having different porosity: Maastrichter (high porous) and Massangis (low porous), loaded with an aqueous solution of an equimolar mixture of sodium sulphate and sodium nitrate. They were subdued to a different relative humidity and to cycles of relative humidity, while the temperature was constantly 20°C. The purpose was to find out more about the performance of salt mixtures in porous materials, as well as to check whether in case of sodium sulphate contamination, the addition of sodium nitrate may be considered as a practice to lower its destructive properties. At 50% RH, the efflorescence of the Massangis sample was consisted mainly of darapskite, indicating a high supersaturation of mirabilite. At 20°C and 85% RH, thenardite formed through the precipitation of mirabilite, was mostly detected in efflorescences of both Maastrichter and Massangis samples. Alternate cycling at 85 and 50% RH led to considerate damage as a consequence of high supersaturation of mirabilite.

Experimental and numerical study on sodium sulfate and chloride crystallization in porous limestone

H. Derluyn¹, R.M. Espinosa-Marzal², P. Moonen¹, J. Carmeliet^{1,2}

Sodium chloride and sodium sulfate are two of the most damaging salts for porous materials. The former is characterized by a single crystal phase, halite (NaCl), while the latter has different crystal phases: thenardite (Na₂SO₄), mirabilite (Na₂SO₄.10H₂0), and heptahydrate (Na₂SO₄.7H₂0). To study their crystallization experimentally, testing is done on Savonnière limestone. This is a quasi-pure calcitic stone with a pore system of micro (0.1 - 10 μ m) and macro pores (100 μ m range). Experimental focus lays on the solid-fluid-crystal interaction, which may result in extensive deformations and damage of the porous material. Therefore, the experimental study looks at the possibilities given by ESEM, DMA and X-ray μ CT to assess deformation and cracking in a qualitative and quantitative way.

The experimental results are indispensable for the development of a physically sound model for salt damage in porous materials. This requires the combination of: (1) a coupled heat, moisture and salt transport model; (2) a crystallization model and (3) a poromechanical model describing the mechanical stresses, induced by the presence of moisture and salt in the pore space of the porous material. In this presentation we focus on the development of a coupled transport and crystallization model within a finite element framework. The transport model combines diffusive and convective transport of the salt ions, taking into account the changed fluid properties due to the salt presence. Many of the thermodynamic salt properties are based on Steiger et al. (2008). The crystallization model uses the kinetic description by Nielsen (1984) for crystall growth. A stable numerical implementation for the physical crystallization/dissolution conditions was found. An outlook to the coupling with the mechanics of deformation and cracking concludes the presented work.

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Growth and dissolution of a loaded KCl crystal: Impact and limit of the supersaturation rate

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Experimentations of crystal growth under constraint made by Becker & Day (1905, 1915), Taber (1916), Correns (1939, 1949) ended in the theory of crystallization pressure. As this theory shows discrepancies with both Riecke's principle and current crystal growth theories, we have performed new experiments in strictly controlled conditions with accurate measuring devices.

A centimetric cubic KCl crystal immersed in a saturated KCl-solution is loaded on its upper face (7KPa). The supersaturation is obtained by inducing water evaporation, which is controlled by buffering the relative humidity (RH) at values under RH-equilibrium of KCl saturated solution (85% at 20°C). The evolution of the crystal in the loaded direction is studied during and after the 300 hours experiments, by different tools including displacement sensors.

At 80% RH and 20°C, the crystal grows inside metastable zone of supersaturation along the unloaded directions. It dissolves along the loaded direction whereas it should have grown also against the load according to the Correns' equation and the supersaturation reached in the solution. Afterwards, we have performed experiments under higher supersaturations by buffering the RH at 60% and 40%. The same dissolution process takes place on the loaded faces. The dissolution rate decreases while the supersaturation increases but neither equilibrium nor growth against the load occurs. At the highest supersaturation rate achieved (40%RH at 20°C), KCl nucleations occur in the solution, decreasing definitively the supersaturation. Because of the narrow metastable zone of KCl crystal, high supersaturation, which would allow crystals to grow and to develop pressure according Correns' equation, is not achievable.

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Porosity and pore structure change in 4D after gypsum crystallization on porous limestones

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Gypsum crystallization on natural building stones due to sulphation processes is a known and widely described phenomenon among researchers. The gaseous SO_2 of the polluted environment reacts with the calcite of the stone, resulting into gypsum ($CaSO_4.2H_2O$) crystallization on the surface and inside the porous structure of the material. In order to obtain quantitative information on porosity and pore structure change before, during and after sulphation processes, the same sample must be considered. The latter is due to the heterogeneity of the pore structure of most rock types by which comparison with the initial state is complex. The problem of most techniques to compare porosity change before, during and after crystallization processes is that most of them are destructive and thus impractical to work with the same sample over a period of time.

With the aid of non-destructive high resolution X-ray computed tomography the researchers of this study investigated different porous limestones and calcareous sandstones before, during and after lab induced gypsum crystallization processes. A full 3D image was obtained during each step of gypsum crust formation with a resolution of 2.5 µm. Besides the visualization of the gypsum crystallization, also quantitative information has been obtained on porosity and pore structure changes. For each stone, radial porosity, open and closed pore structure, partial porosity and distribution of equivalent and maximum opening of the pores has been calculated. The blistering of the gypsum crust on the calcareous sandstone has been quantified and the secondary porosity, due to the dissolution of calcite has been calculated in 4 dimensions. The results of this research are promising for a better understanding of the evolution of pore structure change due to deterioration processes.

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Mitigation Measures and Test Methods for Salt Crystallization in Concrete

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University of Texas at Austin

Salt crystallization deterioration within concrete structures has occurred throughout the entire world with many locations worse than others. Preventative measures and test methods for physical salt attack have not yet been standardized and currently in North America there is a strong push towards determining these standards. Over 40 mortar and concrete mixtures were exposed to laboratory and field testing. Laboratory testing includes controlled temperature cycling of concrete samples in sodium sulfate solution while larger samples are stored in an outdoor sulfate exposure site. Concrete mixtures are tested in a sulfate outdoor exposure site on prisms (75mm X 75mm X 285mm) and 20 L buckets to determine the effectiveness of w/cm, cement types, supplementary cementing materials, and a combination of all these factors on the mitigation of salt crystallization on concrete. The use of lower w/cm and lower C3A cement provide the greatest mitigation efforts towards salt crystallization while mixtures with supplementary cementing materials which have smaller pore sizes do not perform well in salt crystallization tests. These findings along with laboratory testing will be used toward standardizing mitigation measures and test methods.

Precipitation on substrates under mechanical stress – How to resolve 140 years of discussion on Gibbs' thermodynamics

D. K. Dysthe

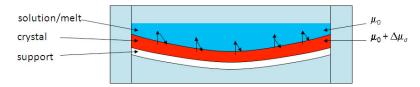
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Thermodynamics of solids subject to non-uniform stresses has been a controversial subject since Gibbs [1]. We have recently performed a series of experiments [2] that seem to contradict theoretical results based on the thermodynamics of non-hydrostatically stressed solids [3-5].

A flat crystal placed on a support is in contact with a saturated solution (they have the same chemical potential μ_0). Then the support is bent and the crystal becomes compressively stressed. The resulting change in the chemical potential of the crystal is $\Delta\mu=(1-v^2)\sigma^2/2E+\gamma\kappa$, where σ is the differential stress parallel to the interface, v is Poissons ratio, E is Youngs modulus, γ is the interfacial tension and E the local curvature of the interface. $\Delta\mu$ causes dissolution of the crystal. However, if the solution volume is finite this will raise the chemical potential of the solution above its equilibrium value μ_0 and this will tend to drive precipitation (growth). If possible, the excess dissolved material will precipitate (grow) on the existing crystal surface. What are the possible final outcomes of this experiment? The lowest free energy end state is clearly complete dissolution of the stressed crystal and growth of a new, unstressed crystal with the same volume and equilibrium crystal shape. What path will the system take and will it ever reach this low energy configuration?

I will explain the experiments and their outcome (initial instability and return to a flat surface) and compare to modeling results based on the thermodynamics of non-hydrostatically stressed solids [3-5] (instability leading to stress corrosion cracking). The focus of the talk is the contradiction between the two results and why it is of both fundamental and applied importance. Then I will propose a possible path to reconcile experiment and theory.

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Crystal Growth in Confinement studied in a model Slit Pore

R. M. Espinosa-Marzal¹, M. Heuberger², J. Carmeliet³

Crystallization pressure is the main reason for the damage caused to porous materials by the in-pore crystallization of salts. Based on the work of *Correns and Steinborn (1939)* it is argued that the pressure relies on ion mobility provided, so the key hypothesis, by the existence of a thin layer of supersaturated electrolyte solution that remains between the crystal and pore wall, which permits the necessary diffusion of the ions to the growing crystal surface. Indeed, the only possible reason for the formation of a liquid film between the confined salt crystal and the pore surface is the action of repulsive surface forces (i.e., disjoining pressure). As far, the growth pressure of a confined crystal has not been directly measured; also the existence of this thin film, and so the validity of this theory has not been proved directly.

The surface force apparatus (SFA) has been successfully used to determine interaction forces between two smooth surfaces in a gas or liquid medium as a function of surface separation. Thus, the major scientific challenge of this project involves the use of this *e*SFA for direct force measurement during crystal growth under non-equilibrium conditions.

We use a model mineral, mica, which is atomically smooth. The salt potassium nitrate (KNO₃) has been selected as our model electrolyte. We investigate the interaction forces between mineral surfaces during approach up to sub-nanometer distances and during separation in low and high concentrated solution, in particular the significance of hydration forces. Besides this, the performed experiments provide information about the structure of the confined liquid. Crystal growth in confinement is detected at the contact region between the mineral surfaces: the displacement of the surfaces during crystal growth can be easily measured and therefore, the action of the crystal growth pressure is demonstrated.

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Effect of crystallization inhibitors on drying behavior of porous building materials

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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. The use of salt crystallization inhibitors has been suggested in the past [1], however with mixed results and as such the suitability of these materials for the treatment of salt damage is still under discussion [2]. Recognizing the need for further information regarding the function of crystallization inhibitors in salt contaminated porous media, their effect on the drying behavior of salinated porous materials has been studied. Drying experiments using potassium hexacyanoferrate (II) trihydrate inhibitor dissolved in 3m NaCl solution were performed and monitored using nuclear magnetic resonance spectroscopy (NMR).

Droplets (300 μ l) of NaCl solution containing different concentrations of crystallization inhibitors were dried on a Polymethyl methacrylate (PMMA) substrate under controlled conditions. Direct imaging of the drying droplet was achieved using a digital microscope to record the onset of crystallization and the crystal morphology. NMR measurements were performed simultaneously to record the solution concentration in the droplet during drying. The results show a delay in crystallization (super-saturation), growth inhibition and a change in crystal morphology in the presence of inhibitor.

Further drying experiments were also performed using brick substrates to determine the effect of the crystallization inhibitor within a porous material. Fired clay bricks saturated with 3m NaCl solution containing different concentrations of inhibitors (0.001m, 0.01m and 0.1m) were dried under controlled conditions. Preliminary results show a faster drying rate and higher super-saturation prior to the onset of crystallization for samples containing an inhibitor. The formation of abundant efflorescence, and alterations in crystal morphology were also observed. The influence of inhibitor concentration on the drying rate and super-saturation was also assessed.

- 1. Rodriguez Navarro, C., Linares-Fernandez, L., Doehne, E., Sebastian, E., Effects of ferro-cyanide ions on NaCl crystallization in porous stone, *J. Cryst. Growth*, 243 (2002) 503-516.
- 2. Lubelli, B., van Hees, R.P.J., Effectiveness of crystallization inhibitors in preventing salt damage in building materials, *Journal of Cultural Heritage*, 8(3) (2007) 223-234.

Predicting water flux through building stones under variable soil, groundwater and climatic conditions.

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Using a full unsaturated flow model and two specially constructed field sites we show how environmental data and a modelling approach can be used to determine moisture movement through building limestone. We focus on a set of stones with variable parameters such as bedding, thickness, foundation, burial depth and location (inland vs coastal) to show how these factors affect the amount of water fluxing through the stone. Using measured evaporation, precipitation and soil moisture content, we explore the effect of rain and driving rain in water transport with the ultimate aim of being able to determine the effects of climate change on stone deterioration. Attention is also paid to the importance of understanding and measuring evaporation rate. In addition we begin to understand which parameters, such as exposure to rainfall and evaporation rate, have the largest impact on water flux which is useful for preventive conservation in terms of shelter design etc. As salts move in solution and chemical processes (calcite precipitation-dissolution etc) are governed by water movement this study gives an estimate of how much salt can be transported through a structure over the course of years. The combination of water transport and evaporation is fundamental to predicting salt crystallisation damage to porous materials.

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Experimental investigation of new techniques for treatment of saltcontaminated masonry

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This poster presents the outline of an ongoing joint research project concerning four potentially interesting treatment methods for salt-contaminated masonry: electrophoresis, crystallisation inhibitors, surface treatment and the creation of salt mixtures. Five types of porous substrate were selected: ceramic brick, three types of French limestones (Massangis, Euville and Savonnières) and calcium silicate blocks, in combination with three sodium salts: Na₂SO₄, NaCl and NaNO₃. Electrophoresis is tested on the chloride, which is the lightest of the anions. Two commercially available inhibitors from mining applications were selected to test their efficiency to prevent crystallisation of the chloride and the sulphate. The proposed surface treatment is a watering treatment with a commercialised fluorosilicate, with the purpose to immobilise present salts or to consume potentially dangerous cations to form fluorides. The option of creating salt mixtures in order to increase the crystallisation relative humidity has already been investigated but found potentially dangerous due to the high solubility of some of the compounds in these mixtures.

Transport parameters of the substrates relative to water and salt solutions are measured using mercury intrusion porimetry, absorption tests, X-ray radiography, vacuum saturation and hygroscopic scanning in order to perform simulations of the selected lab tests. Results of the treatment tests and simulations are expected from 2011.

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Water repellent influence on salt crystallisation in limestone and clay brick

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This presentation focuses on the effectiveness and effects of a water repellent (sodium methylsiliconate in aqueous solution) on salt (14% w/w Na₂SO₄.10H₂O in water) crystallization in Lépine limestone and fired clay brick masonry materials. The methodology adopted in the experimental work presented here is based on capillary rise, concentration by evaporation and consequent crystallization and prevention of efflorescence by the surface treatment.

The results provide strong evidence that treatment with sodium methylsiliconate can have a harmful effect on masonry materials. In fact, the aforementioned water repellent may promote the decay of these materials by suppressing the capillary transport of water and salt solution to their surface, thus forcing the formation of salt crystals in a narrow zone within the pores behind the water repellent which is considerably more damaging than efflorescence (salt growth on the surface).

Localized crystallization within the pores of the test specimens is confirmed by prolonged measurements of capillary absorption of n-heptane through the bottom and top-end surfaces of the specimens and subsequent analysis of the results using the Sharp Front model of absorption into layered composites. Further confirmation comes from synchrotron radiation energy dispersive diffraction tomography experiments.

The use of novel in-situ semi-destructive experimental techniques such as the Drilling Resistance Measurement System (SINT Technology) and the Wombat scratch tool (Epslog Engineering) to map the distribution of crystalline sodium sulphate deposited by evaporation from solution within building and decorative limestones from Cyprus is also investigated.

Deterioration of stone monuments and historical buildings in cold regions

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Stone monuments and historical stone and brick buildings deteriorate due to physical, chemical and biological causes. Among these causes, physical ones such as frost and salt crystallization are quite destructive. In Japan, many stone statues are made of tuff and sand stone, which are relatively soft and porous. During freezing season in winter, pore water in the stone flows to the freezing front to precipitate as ice lens damaging the stone. This mechanism is called frost heaving. This phenomenon can be generally observed in the solidification of liquids in a porous material. The laboratory experiment of freezing pressure showed that the pressure exerted by ice increases with decreasing temperature at the ice front. When crystallization pressure exceeds the tensile strength of the stone, damage (cracking) is caused. During dry season, water migrates to the stone surface and salt accumulates near the surface to cause salt crystallization decay. These processes deteriorate the stone monuments and historical buildings.

In order to develop suitable protective measures to prevent damage, it is necessary to understand the water regime inside the stone monuments and their surroundings. Here, I would like to report on the mechanism of deterioration of stone cultural heritages, experimental study of frost damage, example of the deterioration of stone monuments and stone and brick historical buildings in Japan and their protective measures.

In situ Raman observation of crystallization in mixed Na2SO4-NaNO3 solution droplets

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The basic idea of this research is to use deviations of the crystallization sequence of a salt or a mixed salt solution from the equilibrium pathway as an indicator to detect the degree of supersaturation. This concept is tested with two salt systems, first, the relatively simple and well investigated binary Na2SO4–H2O system and, second, the more complex ternary Na2SO4–NaNO3–H2O system which includes the formation of the double salt darapskite, Na3NO3(SO4)·H2O.

Several double salts have been detected in building materials and most of these salts are incongruently soluble compounds. In contrast to single salts, however, no systematic investigations of the crystallization behavior and deleterious effects of incongruently soluble double salts exist. To assess the damage potential of these salts, a systematic investigation of their highly complex behavior was desirable. Therefore, this presentation deals not only with the crystallization behavior of various solids in pure Na2SO4 but also mixed NaNO3–Na2SO4 solutions.

The sequence of crystals emerging during crystallization at room conditions was determined by using Raman and polarization microscopy. The observed crystallization pathway of sodium sulfates includes the metastable formation of anhydrous Na2SO4 phases III and V. The experimental observations are discussed on the basis of the well known Na2SO4–H2O phase diagram. Due to the lack of a complete NaNO3–Na2SO4–H2O phase diagram, solubilities of stable and metastable phases were calculated using an appropriate thermodynamic model. The experimental results provide clear evidence for crystal growth from highly supersaturated solutions in both systems.

Expansion in OPC caused by sulfate

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The interaction of cement with sulfate solutions leads to expansion. Experimental results and thermodynamic modeling confirmed both the development of a reaction front due to the ingress of sulfate ions. Near the surface ettringite (and gypsum) precipitates. Further within the samples the depletion of portlandite as well as the transformation of AFm into ettringite is observed.

EDX measurements indicated that ettringite precipitates mainly in the C-S-H formed within the boundaries of the former unhydrated clinkers (inner product). The calculated total volume of the solids, even in the areas of maximal ettringite and gypsum precipitation, did not exceed the initial volume of the mortars. These findings indicate that not the overall volume restriction leads to the observed expansion but rather the formation of ettringite within the small pores of the inner product.

Using acoustic emissions techniques to determine new estimators for salt damage in rocks.

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The goal of our study is to find "estimators" of past and future salt weathering of rocks, to know the environmental conditions (mainly relative humidity RH and temperature T) governing salt weathering, in order to predict the future weathering (Grossi et al. 2008). We investigate under which environmental conditions salt will induce damage on rocks. A first approach has been proposed by Benavente et al. 2008 based on an experimental relationship between temperature-relative humidity and crystallization pressure for sodium sulfate, in which they give the T-HR conditions under which crystallization pressure will be higher than 10 MPa.

We propose a new experimental methodology that allows us to record the acoustic emissions (AE) generated during the salt crystallization test. Acoustic emissions are elastic waves generated by crack generation or propagation and have been first applied to salt weathering tests by Grossi et al. 1997. We used different salts: sodium sulfate, sodium chloride, carbonate sulfate and magnesium sulfate. We did the crystallization tests under varying HR-T conditions: HR lower of higher than 80% and T=25°C or 50C°. In order to know the influence of temperature change we did several kinds of experiments. In some experiments we kept RH constant during oven drying and cooling periods and in others we changed the RH conditions, for example HR>80% during drying and HR<80% during cooling and *vice versa*. First results show that carbonate sulfate generates more AE under high RH and sodium sulfate under low RH conditions.

Weathering of the syenite base stones of the Domus Academica

F. A. S. Qvale¹, J. Hutchings¹, D. K. Dysthe².

This case study examines the weathering of the syenite base stones of the Domus Academica of the old University in Oslo. These stones are considerably more weathered than syenite on other buildings in Oslo. The reason for this accelerated decay is explored by field research and laboratory experiments.

Syenite base stones were examined on similar buildings. Differences in sun exposure, salt content and surface treatment were identified. Surface finishing with a bush hammer during quarrying was identified as a cause of micro-fractures in the uppermost surface. This provides pathways for water and salt increasing the action of frost and salt. The relative high concentration of chlorides and sulphates measured in *Domus Academica* compared to similar buildings is linked to the use of de-icing chemicals and acidic cleaning agents. However the damage is significantly greater on the south-face, which is exposed to direct sunlight for most of the year. Rapid and large surface temperature changes were measured, which is thought to be a significant factor in the deterioration observed and is linked to cryptoflorescence, due to increased evaporation within the pores and cracks of the stone.

Laboratory experiments attempted to replicate the mechanisms observed during the field research. Cylindrical syenite samples with different surface treatments were placed in an environmental chamber. The core temperature of the stone, heat radiation hitting the upper surface and salt content was systematically varied. Almost 1000 freeze-thaw cycles of the surface layer were performed. The surface topography and fracture patterns before and after these cycles are described.

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Crystal growth and porosity formation during solvent-mediated phase transformations

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The majority of rocks found at the surface of the Earth are thermodynamically unstable and may be subject to chemical alteration. The presence of a fluid phase allows an easier constituents transport and consequently higher reaction rates. Such reactions are named solvent-mediated phase transformations. In most of the cases the alteration is accompanied by volume changes, which contribute to the porosity of the new-formed material. The questions of crystal growth and porosity formation inside the new-formed material need to be addressed to understand the underlying mechanism of such processes.

We focus on initially nonporous crystals. In that case the porosity formation is a prerequisite, since the new-formed pores allow a transport of the reactive solution through the reacted material up to the interface between the pristine and reacted materials. The KBr-KCl-H2O system is studied as a model system for dissolution/precipitation reaction since reaction is remarkably quick at ambient conditions. The interface between the pristine crystal and the reacted phase is imaged in situ and recorded.

Our observations reveal important insights about the mechanism of porosity formation in solvent-mediated transformations. The reacted phase exhibits a surprisingly organized pattern due to an intimate coupling, localized in space, between dissolution and precipitation. Porosity is strongly heterogeneous and anisotropic, taking the shape of channel-like pores connecting the interface of reaction to the bulk solution.

This study shows that such transformations are self-organizing systems leading to surprising porosity patterns and high reaction rates.

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Crystals at work: Experimental study of the dynamics of single crystal growth under load

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While it is an established idea that growing crystals can set up stresses and be responsible for the breaking apart of rocks, we still lack a basic understanding of how crystals grow against an applied stress. The problem lies at the contact between the crystal and the bearing surfaces, where for growth to take place there must be a liquid film present. The properties of this film are to a large extent unknown. Our objective is to use an experimental approach to obtain a better understanding of this problem.

When a growing crystal lifts an applied load, or just its own weight, the growth on the loaded face(s) is often restricted to a narrow rim. This rim is most likely formed due to limited transport of ions from the bulk into the liquid layer at the contact. If we assume simple diffusion in the liquid layer, and use the thermodynamic dependence on chemical potential of stress, then the width of the rim and the growth velocity in the direction of stress are given by simple relations. By placing a loaded salt crystal in a supersaturated liquid, and observing the size of the rim and the growth velocities in all directions in situ, we can observe how the experimental system agrees with or deviates from the theoretical model. This will provide new insights into the dynamics of crystal growth under applied load, which can be applied when considering how stresses develop due to growing crystals inside rocks.

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The sodium sulfate crystallization pressure as determined from expansion measurements

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In-pore salt crystallization during the weathering is known as one of the main reasons of deterioration of porous materials. One of the most damaging salts in nature is sodium sulfate. The three crystalline phases are known for the sodium sulfate: thenardite (Na2SO4, anhydrous salt), mirabilite (Na2SO4.10H2O) and thermodynamically metastable heptahydrate (Na2SO4.7H2O). The crystalline phase forming in porous materials during the weathering and crystallization pressure being built up represents a big scientific interest both from theoretical and practical point of view.

In present work we study the strain evolution during isothermal and non-isothermal crystallization induced by cooling down bricks saturated with sodium sulfate solution. We use a combination of Nuclear Magnetic Resonance (NMR) and laser distance measurements. Using NMR the concentration was measured in the sample, at the same time using a laser the expansion was measured.

These measurements show a clear correlation between the crystallization and the expansion. Using these measurements, the crystallization pressure for the forming phases can be determined.

Sodium sulfate crystallization induced by drying under wetting – nonwetting conditions, NMR study

T. A. Saidov¹, L. Pel¹, N. Shahidzadeh-Bonn²

The sodium sulfate is recognized as one of the most damaging salts to porous materials. Being able to form three main crystalline phases: thenardite (Na2SO4, anhydrous salt), mirabilite (Na2SO4.10H2O) and the thermodynamically metastable heptahydrate (Na2SO4.7H2O), it still remains a big scientific interest which phase is forming during the drying. In this study we have investigated drying induced crystallization of sodium sulfate salts under wetting and non-wetting conditions.

A setup was used in which Nuclear magnetic Resonance was combined with a digital microscope. Using NMR the concentration is non-destructively determined in a droplet while drying. At the same time using a digital microscope the crystallization is visualized.

These measurements show that under non-wetting conditions the formation of sodium sulfate heptahydrate occurs most preferably, while under wetting conditions the coexistence of sodium sulfate heptahydrate and thenardite is observed.

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Cooling induced formation of sodium sulfate heptahydrate in porous building materials, as studied by NMR

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Salt weathering is widely recognized as one of the most common mechanisms for deterioration of monuments, sculptures and civil structures. One of the most damaging salts is sodium sulfate. Three main crystalline forms can be distinguished for it: thenardite (Na2SO4, anhydrous salt), mirabilite (Na2SO4.10H2O) and the thermodynamically metastable heptahydrate (Na2SO4.7H2O). 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 the present work we focus on the in-pore crystallization of sodium sulfate in vacuum saturated building materials: fired-clay brick, Indiana and Cordoba limestones. Here we use Nuclear Magnetic Resonance (NMR) to measure the hydrogen and sodium content of the sodium sulfate solution, i.e. the concentration of solution can be determined directly within a porous material during the crystallization process. Thereby giving the possibility to directly observe the crystallization kinetics and to obtain information on which crystals are formed. It was observed that during the cooling the metastable heptahydrate is being formed. No spontaneous crystallization of mirabilite was observed.

SalzWiki – A new tool for knowledge transfer and research: A specialized Wiki and Repository on the subject "Salt Decay"

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At a specialist workshop of the German Federal Foundation for the Environment (Deutsche Bundesstiftung Umwelt) in Osnabrück in February 2008, about twenty salt experts from Germany and abroad agreed upon a common initiative to compile a specialist Wiki on salt decay - SalzWiki. As the well known Wikipedia, but only dealing with the specific salt topic and written by researchers, SalzWiki is intended to make current specialist knowledge available to all, to publish research results and practice know-how free of charge. Information can be shared quickly and efficiently, new results of research and practice posted immediately and viewing or editing an article is possible at any place and any time, given internet access.

In addition the repository of SalzWiki serves for experts as a virtual research environment, where they will find the literature not only as full text PDF's but also the scientific primary data behind, not published data, images, diagrams, research papers, etc. The content of SalzWiki will be under editorial supervision and a quick reviewing process ensures the quality of the articles and the data.

Starting with a German version in 2010 an English version is planned to setup in 2011.

All those undertaking research or working in the field of salt decay are welcome to contribute to this joint venture and to collaborate in compiling the SalzWiki.

The current development of SalzWiki is being undertaken as a project of the Hornemann Institute and is co-financed by the German Research Foundation (Deutsche Forschungsgemeinschaft).

Modelling of anhydritic swelling claystones

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Swelling rocks are characterized by the property of increasing their volume when interacting with water. This process constitutes a problem in many engineering fields. In tunnelling, the swelling causes a heave of the tunnel floor, which may impair the serviceability of the structure. When attempting to prevent the heave of the floor by means of an invert arch, socalled swelling pressure develops, which may damage the tunnel lining or cause the tunnel to be lifted as a whole. Swelling rocks are widely distributed, particularly in Switzerland, and have caused serious damage in various tunnels. Particularly problematic rocks are anhydritic claystones, i.e. rocks consisting of clay matrix containing finely distributed anhydrite. Tunnelling in anhydritic claystones is one of the engineering tasks still associated today with large inherent uncertainties, despite over one hundred years of tunnelling activity in such rock. In order to investigate the complex process of swelling, a hydraulic-mechanical-chemical (HMC) coupled model is formulated. The model is based on the continuum-mechanical approach of the theory of mixtures. The main processes considered are the dissolution of anhydrite, the growth of gypsum crystals, diffusive and advective transport and water evaporation. Material-specific, constitutive equations are formulated on the basis of fundamental knowledge about thermodynamics and kinetics of the system water-anhydritegypsum.

Nuclear Magnetic Resonance Studies of Gypsum-based Materials

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This talk will focus on our recent studies of the fundamental mechanisms related to gypsum-based materials using a variety of characterisation tools including nuclear magnetic resonance (NMR), scanning electron microscopy (SEM), and X-ray microtomography (XMT).

The hydration kinetics governing gypsum crystallisation in the two main forms of plaster (α and β) have been studied using rapid NMR relaxation measurements and microscopy techniques. The experimental data reveal significant differences in the gypsum crystallisation kinetics, and hence resultant microstructures, in the two plaster pastes. This work demonstrates the applicability of a combination of these techniques to interpret results from *in situ* NMR monitoring of the gypsum crystallisation process and to characterise the microstructure of the hydrated gypsum which is crucial to the further understanding of mechanical properties (e.g. durability, moisture transport) in these systems. Also, the surface interaction between water molecules and solid gypsum particles has been examined in the presence of additives using rapid two-dimensional T_1 - T_2 NMR relaxation measurements. The ratio of relaxation times T_1/T_2 provides a qualitative description of the surface interactions between water and gypsum. The *in situ* determination of liquid-solid interactions during hydration provides additional information on the behaviour of the additives. The NMR techniques presented are applicable in other building materials and porous media in general.

Localization of crystallization spots at the surface of an internal evaporation front in a model porous medium

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This work focuses on salt transport mechanisms and crystallization localization, resulting from evaporation inside porous media in wick situation. The porous medium is in a vertical position, opened to air at the upper side, sealed laterally and connected to a brine reservoir at the lower side.

Competition between capillarity and gravity forces in the liquid phase stabilizes a heterogeneous front inside the wick. Evaporation occurs at the interface generating a liquid flow from the reservoir to the front, which transports the dissolved salt. This process is studied both experimentally and numerically over a model porous medium.

Results show that the stabilized interface has preferential areas of salt accumulation. The rough front structure imposes that the evaporation rate is heterogeneous, with high evaporation areas in front upper regions and others with low or no evaporation. Consequently, close to front salt transport by convection is locally increased or decreased depending on the evaporation rate, which modifies the liquid flow. Salt preferentially accumulates in the high evaporation rate areas (greater salt convection) leading eventually to a local crystallization. As the evaporation rate distribution is directly linked to the front structure, potential crystallization spots and first crystallization times also depend on the interface characteristics (mean position, width and tortuosity). Simulation results confirm that larger and more tortuous fronts lead to a more rapid crystallization than thinner ones. These results tend to prove that simple 1D models of solute transport in porous media are not well adapted for predicting the onset and the localization of crystallization.

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Some field questions about salt degradation

V. Vergès-Belmin¹, Ph. Bromblet ²

Many efforts have been developed in the last years to understand salt degradation mechanisms. On the other hand, practitioners, in the field, are still having pending questions on what is happening on the buildings they are working on. There is a real need for these endusers to link the results of their measurements and of their observations to possible degradation mechanisms, and get a clearer view on what has been proved and what has not on the topic. In this presentation, we will show the results of the investigations performed on a case study in Poitiers, France, in which the evolution of the degradation patterns does not seem to fit with the theory of salt transport and salt degradation in masonries. We will also show a couple of other strange salt-related degradation patterns and propose to volunteers in the group of experts attending the CRYSPOM workshop to provide possible explanations of these field observations. If some volunteers raise their hand, they will be proposed to work on the topic for one day, and to select among them a spokesman who will present, within the frame of a short presentation, the outcome of their discussions. This exercise will allow a better cross-linking between different specialists and will act as a stimulating and challenging mean to link theory to practice.





Figure 1: A building in Venice, two years apart. Does the reality of the degradation patterns fit to the theory of salt transport and crystallisation

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