SALT DAMAGE OF POROUS MATERIALS: A COMBINED THEORETICAL AND EXPERIMENTAL APPROACH

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Abstract

The paper presents results of an experimental study of the effects of phase transformation processes in porous substrates contaminated with $MgSO_4$. Integral expansion and micro deformation measurements were carried out and scanning electron microscopy (SEM) was applied to explain expansion behavior. Measurements were successfully applied to demonstrate the macroscopic effects of phase changes in the porous material. It could be demonstrated that the integral expansion of the porous substrates is directly reflecting the effect of a particular phase transformation process in the pores and could be reasonably well interpreted on the basis of existing theories of damage mechanisms. In addition, using the cryo-preparation technique (cryo-SEM), it was possible to visualize the various phase transformation steps in the porous substrate. First results using electronic speckle pattern interferometry (ESPI) in order to increase the resolution of the deformation measurements and to obtain position-resolved deformation data were promising and confirmed the dilatometric results.

Keywords: salt crystallization, porous material, dilation measurements, scanning electron microscopy, electronic speckle pattern interferometry,

1 Introduction

It is generally recognized that crystal growth of salts in porous materials is a major cause of damage. However, there is still a controversial debate about the significance of different damage mechanisms. Most often, crystallization and hydration pressures have been mentioned as major causes of decay, but, hitherto, agreement among investigators has not been achieved. In order to provide a better understanding of the underlying processes in porous materials an investigation was initiated considering both, theoretical aspects and novel experimental approaches. This paper presents first results of this work.

Based on thermodynamical considerations common dilatometer measurement were carried out to determine the integral expansion of the samples under significant conditions. In order to obtain more precise information of micro deformations with better lateral resolution the method of electronic speckle pattern interferometry (ESPI) was used. Based on the results of the expansion measurements the optimum point time for taking samples and subsequent SEM analysis was determined.

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2 Experimental

Substrates with well characterized structural parameters were required for the experiments to guarantee that the major effects are caused by the salt crystallization and not by any material change itself. Fritted glass was used as the standard porous substrate in our experiments. This amorphous material offers several advantages including a simple chemical composition and well defined porosities and pore size distributions. Measurements using mercury intrusion porosimetry revealed a median pore radius of 6 μm, and a very narrow pore size distribution for fritted glass specimens (pore class 4) supplied by Schott, Mainz which were used through-out. Porosity was determined to18.3% by optical microscopy and 20% by mercury intrusion porosimetry.

The majority of the experiments were carried out using magnesium sulfate ($MgSO_4$). This salt is known to be deleterious in salt crystallization tests and is subject to a number of different phase changes (deliquescence, crystallization, hydration) depending on temperature and relative humidity (RH). The various phase transitions in the $MgSO_4$–H_2O system allowed for the selection of appropriate experimental conditions in order to initiate phase changes under controlled conditions.

2.1 Dilatometer measurements

Expansion as well as contraction processes were recorded with a dilatometer (DIL 801, Bähr Ltd., Hüllhorst/Germany). The measuring unit consists of an inductive position encoder connected with a quartz rod. Fritted glass plates were cut into prisms with a dimension of 1x1x4 cm^3. These samples were fixed between the rod and a bearing with a constant contact pressure. Deformation of the samples result in a signal of the position encoder, which, enlarged by an amplifier, is transferred to a computer as the recording unit. Thus any length change of the sample is recorded as a one dimensional effect (parallel to the rod) with a high time resolution (experimental details given in Kirchner and Worch, 1993).

First experiments with a single application of 1 ml of a 10 % (w/w) $MgSO_4$ solution (dropped on the center of the prism) and subsequent drying at room temperature did not result in a measurable dilation of the fritted glass sample. Multiple repetition of salt loading seemed to cause a high dilation effect but this was found to be a cross interference. Salt efflorescence at the fixation points of the samples extremely adulterated the pure material expansion. Different attempts, e.g. with a water repellent treatment of sample fixation areas, failed and finally led to a modified drying procedure which prevented the influence of salt efflorescence. Some experiments were performed with an oven enabling a more rapid drying. Salt loading of the samples outside of the dilation measuring unit was another successful attempt. Salt efflorescence was removed from the fixation areas by a mechanical cleaning and proper samples were introduced into the machine. Dilation effects of a secondary loading, e.g. further application of solution or exposure to humid air could be detected without any interference.

2.2 Examination with scanning electron microscopy

Scanning electron microscopy with cryo-preparation was used as an adequate tool to visualize processes in the pores. Temporary phase conditions can be studied without artifacts and with high resolution even in the sub-microscopic range. Regarding examinations with a common scanning electron microscope samples have to be stable inside the applied vacuum, with cryo-preparation any existing humidity resp. pore solution are frozen without ice crystallization or drying artifacts and can be analyzedconfidently under vacuum conditions of the microscope. A solution forms an amorphous (glassy) solid when splat cooled with rates > 1000 K/s and will not change its appearance. To receive such high cooling rates, smelting nitrogen (so called Slush-N_2) is used as cooling resource. Glassy frozen samples are fixed on a cooling tablet inside of the microscope and examined at a temperature of about -150°C. The method is described more detail by Langenfeld et al. 1994.

Cryo-examination offer the great advantage that ordinary fluctuations of ambient conditions do not affect samples during microscopic analysis. Fixed sample condition can be examined without pressure of time.

2.3 ESPI measurements

To get further insight in the phase transition process of the investigated salt, especially to detect areas on the surface of the glass substrate, where phase changes start to produce micro-deformations, measurements were performed using ESPI. This laser-optical method, which is comprehensively described in literature (e.g. Sirohi, 1993) has proven to be a powerful tool in the study of minute surface deformations down to the sub-micron range. Its main advantages are that displacements can be measured without mechanically contacting the specimen, spatially resolved within the field of view, and with high resolution. In contrast to the dilatometer method, which measures the integral deformation of a whole specimen, ESPI measurements can identify parts of the surface that deform due the onset of pressure. It is intended to combine these measurements with cryo-SEM examinations and to analyze such deformed regions in detail. It should thus be possible to visualize the deformation producing salt crystals directly and to study their morphologies and temporal behavior.

Just as in the dilatometer measurements severe problems occurred during phase transition due to the efflorescence of salt. This led to a change in the micro-topography of the specimen and thus to significant alteration of the light field scattered from the object which was not caused by a displacement of the object surface. Again, special drying procedures were applied to minimize this effect.

3 Experimental results and discussion

Experiments followed a methodical chain. Thermodynamic calculations as a first step provided basic information on the salt systemconsidered (here $MgSO_4$–H_2O). These data were used to select appropriate ambient conditions for the dilatometric measurements. In order to provide an optimum interpretation of the observed length changes sampling for the cryo-SEM examinations took place where peaks or strong gradients etc. in the dilation records were indicating an active phase transition process. For detailed information of surface deformation processes ESPI measurements were performed regarding the previous data.

3.1 The system $MgSO_4$–H_2O

The phase diagram of the $MgSO_4$–H_2O system is depicted in Fig. 1, where only the stable phases in the temperature range from about 0–100 °C are considered. Close to room temperature epsomite ($MgSO_4 \cdot 7H_2O$) is the stable form in the presence of liquid water. Under dry conditions epsomite can dehydrate to form hexahydrite ($MgSO_4 \cdot 6H_2O$) and, finally, the monohydrate kieserite ($MgSO_4 \cdot H_2O$). At room temperature the dehydration of epsomite occurs, if the relative humidity (RH) drops below 51%. Further dehydration to kieserite requires relative humidities below 42%. These values are increasing with temperature, for instance, at 40 °C, the equilibrium dehydration humidities of hexahydrite and epsomite are 72% and 53%, respectively. At temperatures above 47.5 °C hexahydrite rather than epsomite is the stable solid in presence of liquid water. Dehydration of hexahydrite at that temperature occurs at 70% RH.

In the discussion so far, we assumed full equilibrium, i.e. the occurrence of metastable phases was not considered. It is well known however, that there are a number of additional metastable hydrates in the $MgSO_4$–H_2O system. Apart from the tri-, tetra- and pentahydrates $MgSO_4 \cdot 3H_2O$, $MgSO_4 \cdot 4H_2O$, $MgSO_4 \cdot 5H_2O$, there is a well characterized $MgSO_4 \cdot 1.25H_2O$ and a second lower hydrated form with a composition close to the dihydrate (von Hodenberg and Kühn, 1967). For example, drying of a $MgSO_4$ solution at 200 °C in a desiccator cabinet for several days did not yield kieserite which would be the stable phase, but rather a mixture of different lower hydrated forms including $MgSO_4 \cdot 1.25H_2O$. Hence, the temperature and RH conditions during our experiments might also lead to the formation of metastable phases. Nonetheless, the drying conditions realized in the experiments will cause the formation of lower hydrated forms of $MgSO_4$, though not necessarily the thermodynamically most stable form. If these solids get in contact with liquid water at room temperature, they will dissolve and the resulting solution will be considerably supersaturated with respect to epsomite. Hence, crystallization and growth of epsomite occurs under conditions of high supersaturation and as a growing crystal becomes confined in the pore space a high crystallization pressure can build up.

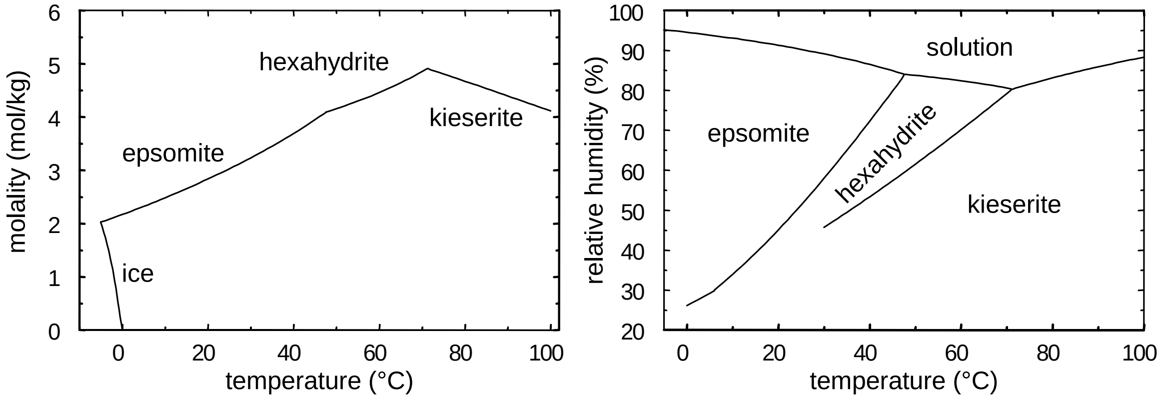

Figure 1: Solubilities of magnesium sulfates (left) and temperature–humidity diagram (right) of the $MgSO_4$–H_2O system

3.2 Material deformation caused by the system $MgSO_4$–H_2O

A fritted glass sample saturated with 1ml of 10 % (w/w) $MgSO_4$ solution and dried (ring oven) up to 60 °C (steps of 10°C hold for 6 hours; temperature cycle passed through for two times) shows a length change given in Fig. 2. The course of the dilation curve, which is relatively complex, can be explained by three main factors: a) a thermal dilation of the substrate, b) dilation caused by salt crystallization and c) dehydration of salt to lower hydrated forms linked with a reduction of the volume and thus a reduction of salt initiated dilation. As a similar temperature/dilation curve has been recorded without application of salt solution we were able to compensate temperature induced length change.

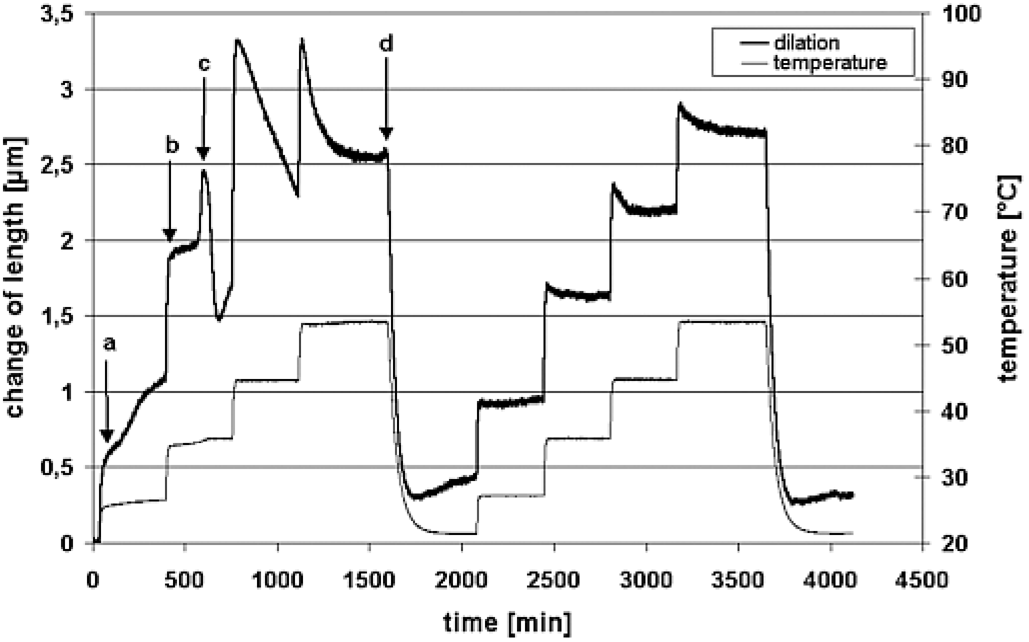

Figure 2: Dilation of a fritted glass sample loaded with 1ml 10% (w/w) MgSO4 solution and heated stepwise to 60 °C (oven temperature, two cycles shown)

Cryo-SEM offers a clear interpretation of the curve lapse. Application of the magnesium sulfate solution immediately results in an almost completely filled pore space as the fritted glass has high capillary forces (Fig. 3).

Increase of temperature up to 30 °C causes a fast thermal dilation of the substrate (point (*a*) in Fig. 2). With beginning evaporation the salt solution becomes more concentrated and the crystallization of epsomite ($MgSO_4 \cdot 7H_2O$) starts. This is linked to a further smooth increase of the dilation curve within the 30 °C temperature stage. Temperature increase to 40 °C again causes a fast thermal dilation intensifying the effect of the crystallization process (point (*b*) in Fig. 2). Growth of epsomite crystals starts at the pore walls and, finally, the entire pore space is filled. The cryo-microscopic picture clearly demonstrates that further drying of the sample causes a dehydration of the water rich salt phase. Drying cracks evolve at the grain boundaries of the epsomite crystals and the total volume of the saltphase is reduced (Fig. 4)

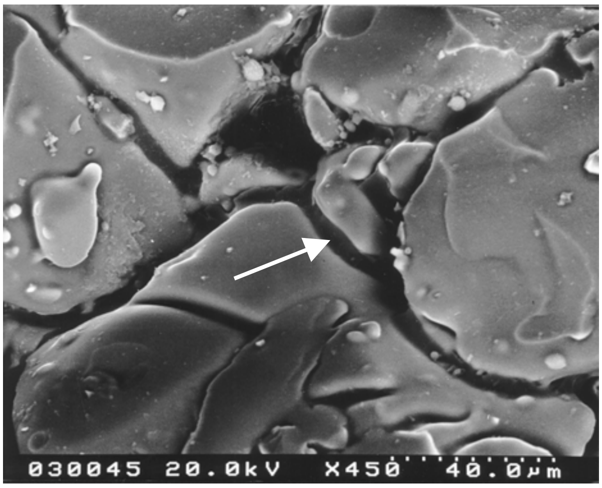

Figure 3: Pore space is completely filled immediately after impregnation with $MgSO_4$ solution (dark liquid, see arrow)

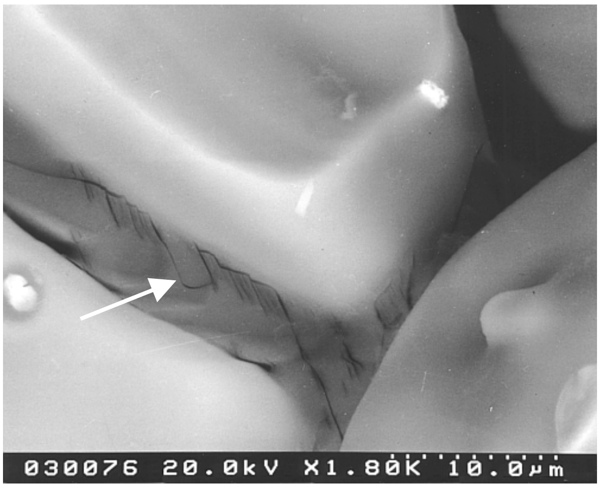

Figure 4: Formation of epsomite complete; further drying causes dehydration cracks along the salt crystal boundaries (see arrow).

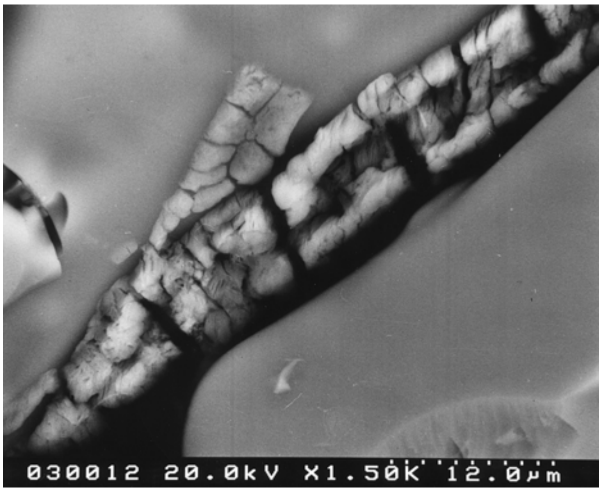

Figure 5: At the final drying stage the sample contains a salt matrix consisting of low hydrated $MgSO_4$-H_2O penetrated by micro cracks.

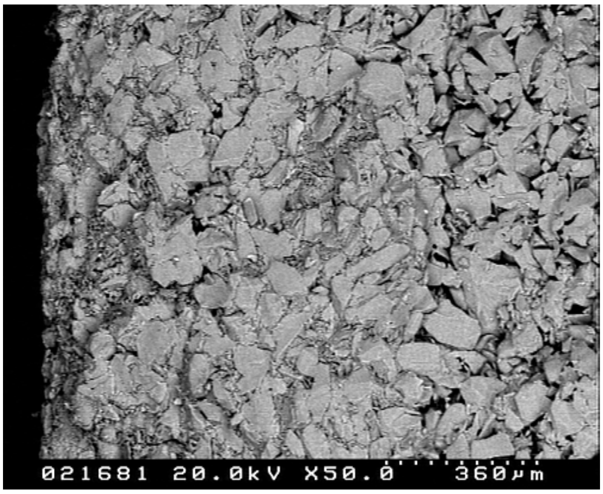

Figure 6: After repeated cycles of salt loading the surface zone is completely filled with crystalline salt (surface left).

The dilation curve (Fig. 2) reflects SEM observations. At the 40 °C stage a sudden decrease of the sample length is recorded (point (*c*) in Fig. 2). We assume that dehydration is starting in the surface zone of the sample that time. The drying process however will not proceed in a similar way over the entire sample. Salt crystallization in the outer zone will reduce water transport to the surface. Not until dehydration occurs it will get more permeable resulting in a better transport to the surface and also in further crystallization process in the inner zone. Thus, there is not only one crystallization/dehydration peak in the dilation curve but there are at leasttwo or three. Interference of salts in the inner and outer parts of the sample is however not finally investigated. At the end of the 60 °C stage (point (*d*) in Fig. 2) the dehydration process is finished (regarding chosen conditions).

The microscopic picture shows several micro cracks penetrating the salt matrix and enormously increasing the inner surface (Fig. 5). A repetition of the temperature cycle only just demonstrates the thermal dilation of the substrate. Thermal length change is however less intense in each temperature step compared to a none-loaded sample. Microscopic examinations show a very inhomogeneous distribution of the salt along the sample cross-section. There is a distinct compaction zone at the surface where the pore space is completely filled with salt (Fig. 6). The thickness of this zone is obviously influenced by the condition ofthe material’s pore space. The same experimental conditions resulted in a compaction zone of about 1.0 mm for the fritted glass material and about 0.3 mm for corundum which was also tested (porosities: fritted glass = 20% (v/v), corundum = 24% (v/v)).

A secondary humidification (by salt solution or even by humid air) of pre-loaded samples with low-hydrated $MgSO_4$ (repeated soaking of salt solution followed by intensive drying at 200 °C outside of the measuring apparatus) will yield a supersaturated condition with respect to epsomite (Fig. 1). Hence, epsomite will crystallize spontaneously requiring significant space. By further addition of water the salt will be re-dissolved. This process could be validated in dilation experiments by either adding 1ml of 10 % (w/w) $MgSO_4$ solution, or, by storage in humid air (RH > 95 %). The addition of liquid water results in a quite fast reaction within only a few minutes (Fig. 7). The interaction with humid air shows in a very similar dilation course but requires much more time (Fig. 8).

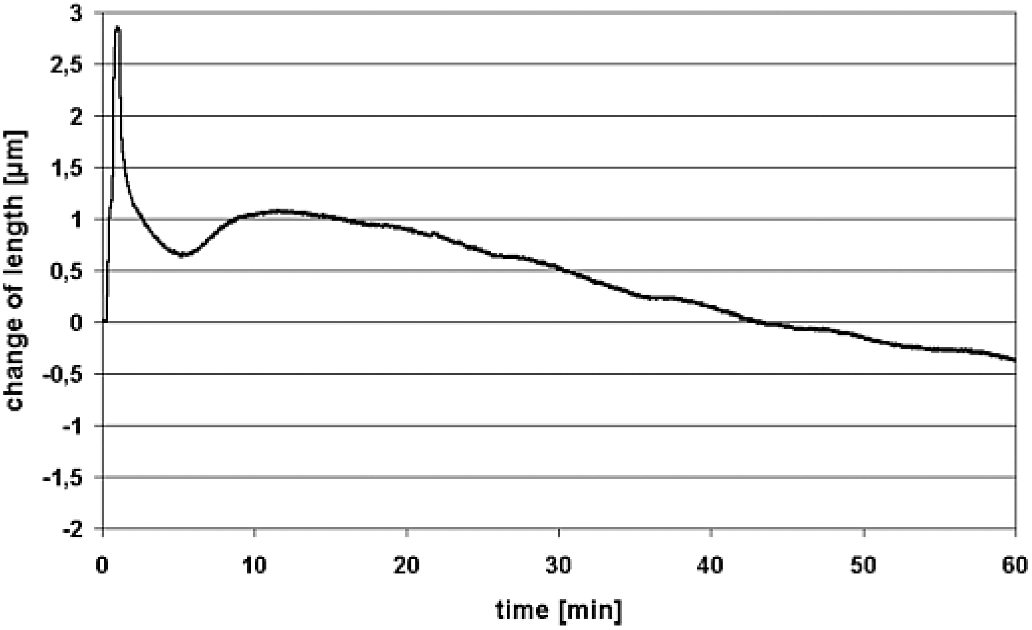

Figure 7: Humidification of pre-loaded and dried (60 °C) fritted glass samples by 1 ml of 10 % (w/w) $MgSO_4$ solution.

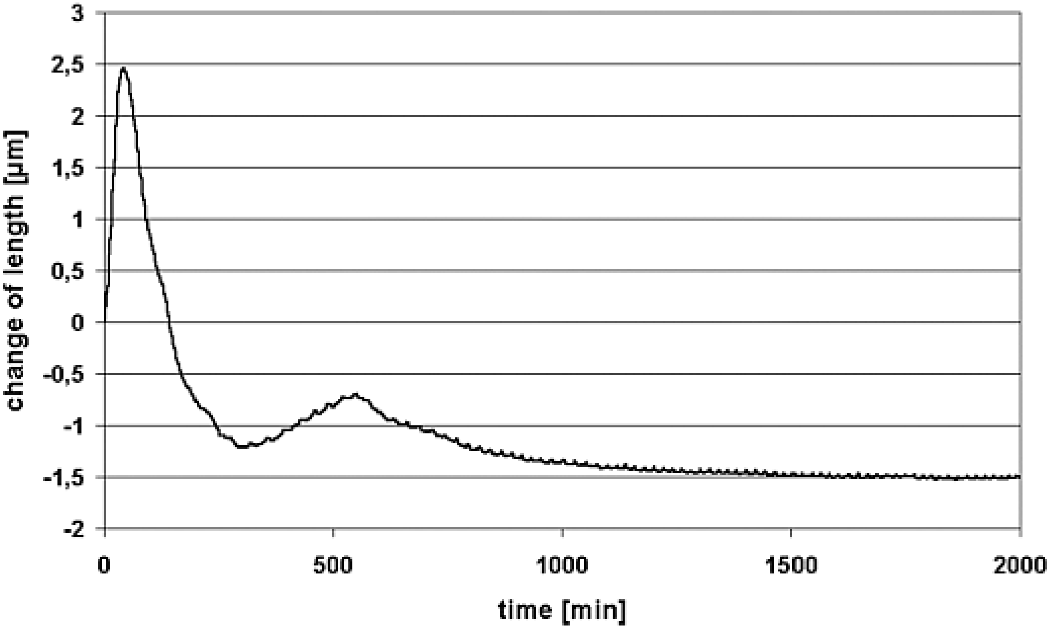

Figure 8: Humidification of preloaded and dried (200 °C) fritted glass samples by storage in humid air (RH > 95 %)

Both experiments show a significant increase and spontaneous decrease in sample length (crystallization of epsomite and dissolution of the salt). The second short increase may be caused by hydration effects from the inner part of the samples. The measurable length decrease below the zero level can be explained by the initial dilation amount of the preloaded samples given by the crystal growth in the preparation process.

In first ESPI-measurements the transition from low hydrated $MgSO_4$, probably mainly kieserite to a high hydrated form, probably epsomite was investigated, too. A small cube of fritted glass with dimensions of about (1 cm^3) was soaked with $MgSO_4$ solution until saturation and dried afterwards in the same manner as in the dilatometer measurement (several hours at 200°C in an oven). During the following ESPI measurements the specimen was inserted in a small climatic chamber, where the temperature and the humidity of the ambient air can be controlled by a computer. A phase transition within the substrate was induced by stepwise increasing the air humidity in the climatic chamber from 25% RH to 85% RH within a time period of about 20 hours. The air temperature during the measurement was kept constant at about 27°C.

The main results of this first measurement can be summarized as follows: in the beginning of the experiment almost no deformation within the investigated area could be observed. The situation changed significantly when the relative humidity was increased to about 43%. Now, first sub-areas underwent displacements, indicating the onset of pressure induced deformation. It can be seen from Fig. 1 that this in agreement with the theoretically predicted humidity value, where a phase transition should occur. Although the final value of 85% RH was reached about 13 hours later the amount of deformation increased for about 16 hours, then slowed down and stopped after about 17 hours. In contrast to the dilatometer results no decrease of deformation was registered in this experiment because the RH was increased to only RH 85 %. Thus, humidity was too low for a substantial dissolution of epsomite at room temperature (see Fig.1).

More details of these ESPI measurements can be found in a separate paper within this proceedings volume.

4 Conclusions

Based on a thermodynamic analysis of the phase behavior of salts, the measurement of both, integral dilation and micro-deformation in combination with the cryo-SEM visualization of micro structural provides a helpful tool to investigate the effects of crystal growth in porous materials.

The results presented in this paper build a first step to develop a more detailed understanding of salt damage in porous materials. Existing data already underline material loading caused by steady expansion and shrinkage processes as a results of phase changes within the pore space. Future work will have to include different phase transformation processes under varying experimental conditions. It will also be necessary to extend this work to other types of substrates as well as other salts.

Acknowledgement

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References

Kirchner D., Worch A. 1993. Physikalische Vorgänge bei der Salzkristallisation. Bautenschutz Bausanierung 7, 101-103

Langenfeld M., Juling H., Blaschke R. 1994. Kryo-Untersuchungen zum Feuchtigkeits- und Salztransport in porösen Baustoffen. Wiss.Z.Hochsc.Archit.Bauwes.–Weimar 40, 23-26.

Sirohi, R.S. 1993. Speckle Metrology, Marcel Dekker, New York

von Hodenberg R., Kühn R. 1967. Zur Kenntnis der Magnesiumsulfathydrate und der Effloreszenzen des Kieserits von Hartsalzen. Kali u. Steinsalz 4, 326–340.