Deformation and damage due to drying-induced salt crystallization in porous limestone

Hannelore Derluyn^{a,b,*}, Peter Moonen^{a,b}, Jan Carmeliet^{a,b}

^a*ETH Zurich, Chair of Building Physics, Wolfgang-Pauli-Strasse 15, 8093 Zürich, Switzerland*

^b*EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Building Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland*

Abstract

This paper presents a computational model coupling heat, water and salt ion transport, salt crystallization, deformation and damage in porous materials. We focus on crystallization-induced damage. The theory of poromechanics is employed to relate stress, induced by crystallization processes or hygro-thermal origin, to the material's mechanical response. A non-local formulation is developed to describe the crystallization kinetics. The model performance is illustrated by simulating the damage caused by sodium chloride crystallization in a porous limestone. The results are compared with experimental observations based on neutron and X-ray imaging. The simulation results suggest that the crystallization kinetics in porous materials have to be accurately understood in order to be able to control salt dam-

*Corresponding author: tel: +41 58 765 4722; email: hderluyn@gmail.com;
address until 30 Sep.'13: EMPA Dübendorf, Überlandstrasse 129, 8600 Dübendorf, Switzerland

address from 1 Oct.'13: Ghent University, Department of Geology and Soil Science - UGCT, Krijgslaan 281, S8, 9000 Gent, Belgium

Email addresses: hderluyn@gmail.com (Hannelore Derluyn),
moonen@arch.ethz.ch, peter.moonen@empa.ch (Peter Moonen),
carmeliet@arch.ethz.ch, jan.carmeliet@empa.ch (Jan Carmeliet)

age. The results show that the effective stress caused by salt crystallization depends not only on the crystallization pressure but also on the amount of salt crystals, which is determined by the spreading of crystals in the porous material and the crystallization kinetics.

Keywords: salt crystallization, A. fracture, B. porous material, C. finite elements, C. nondestructive evaluation

1. Introduction

Water and dissolved salt ions may penetrate into building materials due to diffusive and advective transport. Upon changes in the environmental conditions, salt can crystallize at the surface (efflorescence) or inside the material (subflorescence). Subflorescence is accompanied with the development of crystallization pressures, which may lead to spalling and cracking of the material, and thus to a reduction of the lifetime of a construction or monument. Until now, the mechanism of crystallization in confined conditions and the related damage processes, as well as the computational modeling, are still subject of scientific analysis. The availability of a model providing full coupling between heat-water-salt ion transport, salt crystallization, deformations and damage would however be an important asset for engineers and conservators. It would allow them to assess and compare different maintenance, repair or conservation techniques or to assess the durability of a new building material under different climatic conditions, without having to perform long-term experiments.

Coupled numerical models for heat-water-salt transport and salt crystallization in building materials have been developed and described in the

19 literature (Espinosa et al., 2007; Nicolai et al., 2007; Koniorczyk, 2012). The-
 20 ories defining the crystallization pressure that is exerted when salt crystals
 21 grow in confined conditions are described as well (Scherer, 1999; Flatt, 2002;
 22 Steiger, 2005a,b; Coussy, 2006). Moonen et al. (2010, 2011) developed a
 23 model that covers the effect of thermal and hygric changes on the damage
 24 behavior of porous media. There remains however a need for bringing to-
 25 gether the available approaches within a single unifying framework. It is
 26 especially challenging to formulate the coupling between salt crystallization
 27 and the mechanical response of the building material and to accurately model
 28 the crystallization kinetics in a physically and numerically sound way.

29 In the next section, we present a fully coupled model for heat, water and
 30 salt ion transport, salt crystallization, material deformation and damage in
 31 porous media. We briefly recall the modeling of heat and moisture transport
 32 (Derluyn, 2012). The modeling of the salt crystallization process, the cou-
 33 pling with the mechanical behavior and the damage criterion are discussed in
 34 more detail. In section 3, we summarize experimental observations of damage
 35 caused by sodium chloride crystallization, induced by drying of an initially
 36 wet limestone (Derluyn, 2012). The material and salt properties, needed
 37 as input for the model, are also given. Section 4 comprises the simulation
 38 of the performed experiment. Comparison with the experimental data sug-
 39 gests that the crystallization kinetics play an important role in the accurate
 40 prediction of salt damage.

2. A coupled model for transport, crystallization, deformation and damage

2.1. Conservation of mass

We consider the porous medium consisting of a superposition of four phases: (1) the solid material matrix, (2) the gas phase, (3) the liquid phase and (4) the crystal phase. In these phases several components can be present. For the gas phase we consider dry air and water vapor, for the liquid phase water and dissolved salt ions. Exchange of water can occur between the liquid and the gas phase due to evaporation or condensation, or between the liquid and the crystal phase when hydrated salt crystals form or dissolve. Exchange of salt ions occurs between the liquid and the crystal phase when crystals precipitate or dissolve. We assume that the dissolved salt does not separate macroscopically in the absence of an electric field. Thus the cations and anions are always transported jointly.

We further assume that the solid phase does not exchange mass with other phases. We consider the gas pressure, p_g , to be constant and equal to the atmospheric pressure. In addition, we consider changes in the water vapor mass to be negligible with respect to changes in the liquid water mass and we assume that salt crystals do not move in the pore space.

Under these assumptions, the mass balance is expressed by:

$$\Phi \frac{\partial (S_l \rho_l + S_{cr} \rho_{cr})}{\partial t} = \nabla \cdot (\mathbf{K}_l \nabla p_c + \boldsymbol{\delta}_v \nabla p_v) \quad (1)$$

with Φ the total accessible porosity, S_l and S_{cr} the liquid and the crystal saturation degree, and ρ_l and ρ_{cr} the density of the liquid phase and of the salt crystal. $\mathbf{K}_l$ is the liquid permeability as function of capillary pressure p_c .

64 The capillary pressure expresses the pressure difference across the liquid-gas
 65 interface and is defined as:

$$p_c = p_l - p_g \quad (2)$$

66 with p_l the liquid pressure and p_g the (constant) gas pressure. δ_v is the
 67 vapor permeability in function of vapor pressure p_v . The vapor pressure can
 68 be expressed in terms of the capillary pressure p_c , the absolute temperature
 69 T and the water activity a_w by the modified Kelvin relation:

$$p_v = a_w p_{v,sat} \exp\left(\frac{p_c}{\rho_w R_v T}\right) \quad (3)$$

70 with $p_{v,sat}$ the saturated vapor pressure, ρ_w the water density and R_v the
 71 gas constant for water vapor. The water activity depends on the temper-
 72 ature and the salt concentration and accounts for the change of the vapor
 73 pressure in equilibrium with a salt solution, compared to the vapor pressure
 74 in equilibrium with pure water. For pure water, the water activity equals 1.
 75 The higher the salt concentration gets, the lower the water activity will be,
 76 leading to lower vapor pressures.

77 Under the assumption that the dissolved salt ions are transported to-
 78 gether, the mass balance for the salt dissolved in the liquid phase reads:

$$\Phi \frac{\partial (S_l \rho_l C)}{\partial t} + \Phi \frac{\partial S_{cr} / \bar{V}_{cr}}{\partial t} = \nabla \cdot (\rho_l \mathbf{D}_i^l \nabla C) + \nabla \cdot (C \mathbf{K}_l \nabla p_c) \quad (4)$$

79 with C the salt concentration in mole/kg liquid solution and $\bar{V}_{cr}$ the molar
 80 volume of the salt crystal. $\mathbf{D}_i^l$ is the salt diffusion coefficient in the liquid
 81 phase.

82 2.2. Conservation of energy

83 The global energy balance for the porous medium reads:

$$\begin{aligned} & \frac{\partial \left(\left((1 - \Phi)c_{p,s}\rho_s + \Phi c_{p,l}S_l\rho_l + \Phi c_{p,cr}S_{cr}\rho_{cr} \right) (T - T_0) \right)}{\partial t} + \\ & \frac{\partial \Phi L_{cr}S_{cr}\rho_{cr}}{\partial t} + \nabla \cdot \mathbf{q}_e = 0 \end{aligned} \quad (5)$$

84 assuming that the enthalpy of water vapor and of dry air are negligible for the
85 application of our model (Janssen, 2002). $c_{p,s}$, $c_{p,l}$ and $c_{p,cr}$ are the specific
86 heat capacities at atmospheric pressure of the solid phase, the liquid phase
87 and the crystal phase, respectively. ρ_s is the density of the solid material
88 matrix, L_{cr} the heat of crystallization and T_0 the reference temperature for
89 the enthalpy, being 0°C (273.15 K).

90 The heat flux $\mathbf{q}_e$ is a combination of a conductive part and an advective
91 part. The conductive part is given by Fourier's law:

$$\mathbf{q}_{e,c} = -\boldsymbol{\lambda} \nabla T \quad (6)$$

92 with $\boldsymbol{\lambda}$ the apparent thermal conductivity of the porous material. The ad-
93 vective part is described as:

$$\mathbf{q}_{e,a} = - (c_{p,v} (T - T_0) + L_v) \boldsymbol{\delta}_v \nabla p_v - c_{p,l} (T - T_0) \mathbf{K}_l \nabla p_c \quad (7)$$

94 with $c_{p,v}$ the specific heat capacity of water vapor and L_v the latent heat of
95 evaporation of water.

96 2.3. Salt crystallization

97 The salt crystal mass balance reads:

$$\Phi \frac{\partial (S_{cr}\rho_{cr})}{\partial t} = e_{crl} \quad (8)$$

98 where we have to define the mass exchange e_{crl} between the liquid and the
 99 crystal phase. This mass exchange is described by the kinetics of salt crys-
 100 tallization or dissolution. It is assumed that the supersaturation U is the
 101 driving force for crystallization, and consequently that the mass exchange
 102 during crystallization is given by (Espinosa et al., 2008; Koniorczyk, 2010):

$$e_{crl} = \zeta K_{m,cr}(U - 1)^{g_{cr}} \quad \text{for } U > U_{thr} \quad (9)$$

103 where $K_{m,cr}$ and g_{cr} are kinetic parameters and ζ is the fraction of the cap-
 104 illary active pore space filled with salt solution. In order for new crystals to
 105 nucleate and grow, the supersaturation has to exceed a threshold value U_{thr} .

106 Dissolution is described by a similar type of equation, only the kinetic
 107 parameters and the threshold value differ:

$$e_{crl} = -\zeta K_{m,diss}(1 - U)^{g_{diss}} \quad \text{for } U < 1 \quad (10)$$

For the modeling of the crystallization, besides the kinetics, also the avail-
 ability of pore volume space needs to be considered. If no space is available
 for crystals to grow, crystallization will stop and consequently the concen-
 tration in the solution will remain higher than when the crystals could grow
 freely. Moreover, dissolution can only take place as long as there are crys-
 tals present. Finally, the presence of crystals at a certain location influences
 nucleation and growth of crystals at neighboring locations. In order to get
 a stable numerical method incorporating all these constraints, the mass ex-
 change term e_{crl} is implemented as:

$$\begin{aligned} e_{crl} = & f(S_{cr}, 1) \cdot \zeta K_{m,cr}(\max(U, U_{thr}) - U_{thr})^{g_{cr}} + \\ & f(S_{cr}, 0) \cdot \zeta K_{m,diss}(1 - \min(U, 1))^{g_{diss}} \end{aligned} \quad (11)$$

108 where the first term represents crystal growth and the second term represents
109 crystal dissolution.

110 The function f is introduced to ensure that:

- 111 1. Crystallization stops when the available pore volume is occupied by
112 salt crystals: as long as $S_{cr} < 1$, $f(S_{cr}, 1)$ equals 1 and the crystalliza-
113 tion kinetics are active. When the pore volume is filled with crystals,
114 $S_{cr} = 1$, no crystallization occurs anymore and consequently $f(S_{cr}, 1)$
115 equals 0.
- 116 2. Dissolution can occur as long as there are still crystals present: as long
117 as $S_{cr} > 0$, $f(S_{cr}, 0)$ equals -1. When all crystals are dissolved and
118 $S_{cr} = 0$, the dissolution kinetics stop and $f(S_{cr}, 0)$ equals 0.

119 Physically, we would only need a step function to define f . However, as
120 step functions may introduce numerical problems due to their discontinuous
121 nature, we smooth the function f by means of an exponential function:

$$f(x_1, x_2) = \text{sgn}(x_2 - x_1) \cdot \left(1 - \exp\left(-\left|\frac{x_1 - x_2}{HBW}\right|\right) \right) \quad (12)$$

122 where $\text{sgn}()$ represents the signum function, x_1 and x_2 are values, and HBW
123 is a parameter controlling the width over which the step is smeared in
124 the function f . The half-band-width HBW of this function is taken low
125 ($HBW=0.01$) in order to assure that the exponential function rapidly ap-
126 proaches zero as the difference $|x - r|$ increases and that the function f ap-
127 proximates as close as possible a step function.

128 The function U_{thr} is defined as:

$$U_{thr} = 1 + (U_{start} - 1) \cdot \exp(-v\bar{S}_{cr}) \quad (13)$$

129 and represents the drop of the crystallization threshold from U_{start} to 1. For

130 primary crystallization (i.e. if no crystals are present) the supersaturation
 131 has to exceed the supersaturation value U_{start} before crystallization starts.
 132 The drop from U_{start} to 1 is related to the nucleation and growth kinetics.
 133 The nucleation and growth kinetics determine how long a certain supersaturation
 134 U is maintained until a sufficient amount of crystals have nucleated
 135 and/or sufficiently large crystals have grown so that new crystals start to
 136 grow at lower supersaturation levels. These phenomena are incorporated in
 137 the parameter v and the function $\bar{S}_{cr}$. $\bar{S}_{cr}$ is a measure for the amount of crystals
 138 in the immediate neighborhood, influencing the crystallization kinetics
 139 at the location being evaluated. v quantifies how important the presence of
 140 already formed crystals is on the crystallization threshold U_{thr} . A non-local
 141 formulation is developed for the function $\bar{S}_{cr}$, defining $\bar{S}_{cr}$ as:

$$\bar{S}_{cr} = \frac{\int_{\Omega} w_f S_{cr} d\Omega}{\int_{\Omega} w_f d\Omega} \quad (14)$$

142 with w_f a weighting function, defined as a multivariate normal distribution:

$$w_f = \frac{1}{(2\pi)^{\frac{k}{2}} l^k} \exp\left(-\frac{r^2}{2l^2}\right) \quad (15)$$

143 with r the distance away from the evaluated point and l the influence length.
 144 k represents the number of dimensions (1, 2 or 3). The influence length l
 145 controls the extent of the crystallization zone. The smaller the value for l is,
 146 the more localized crystallization will be; larger l -values lead to crystallization
 147 that is more spread over the domain Ω .

148 2.4. Conservation of momentum

149 The solid momentum balance, in absence of body forces, reads:

$$\nabla \cdot \boldsymbol{\sigma}_s = 0 \quad (16)$$

150 with $\boldsymbol{\sigma}_s$ the partial stress tensor, expressed as:

$$\boldsymbol{\sigma}_s = \boldsymbol{\sigma} - bp_s \mathbf{I} \quad (17)$$

151 with $\boldsymbol{\sigma}$ the effective stress tensor, b the Biot coefficient, p_s the solid pressure
 152 and $\mathbf{I}$ the second order unit tensor. p_s accounts for the mechanical effects of
 153 the constituents in the pore space on the macroscopic behavior of the porous
 154 material. The Biot coefficient is defined as:

$$b = 1 - \frac{\tilde{K}}{\tilde{K}_s} \leq 1 \quad (18)$$

155 with $\tilde{K}$ the bulk modulus of the porous material (solid matrix and pore
 156 space) and $\tilde{K}_s$ the bulk modulus of the solid matrix.

157 The solid pressure is defined according to the theory of poromechanics
 158 (Coussy, 2004, 2010):

$$p_s = \sum_j [S_j (p_j - p_{0,j})] \quad (19)$$

159 where j represents the different phases present in the pore space, being gas,
 160 liquid and crystal. p_j is the pressure exerted by phase j and $p_{0,j}$ is the pressure
 161 which accounts for the averaged pressure shift induced by the interface stress,
 162 $2\sigma_{s,j}/r$, between the phase and the solid matrix, with respect to the possible
 163 values of the pore radius r (Coussy, 2010). The pressure $p_{0,j}$ is expressed as
 164 (Coussy, 2010):

$$p_{0,j} = \frac{1}{S_j} \int_0^\infty \frac{2\sigma_{s,j}}{r} \frac{dS_j}{dr} dr \quad (20)$$

165 It is generally assumed that there is a thin liquid film between the salt crystal
 166 and the solid matrix (see Figure 1) (Scherer, 2004; Steiger, 2005a). Thus there
 167 is no direct interface between the salt crystal and the solid matrix. Therefore,
 168 we assume that we can omit the interfacial stress between the crystal phase

169 and the solid phase ($p_{0,cr}$) and we consider only the interfacial stress between
 170 solid and gas phase and solid and liquid phase, $p_{0,g}$ and $p_{0,l}$, respectively.
 171 The solid pressure is then expressed as:

$$p_s = S_g p_g + S_l p_l + S_{cr} p_{cr} - S_g p_{0,g} - (S_l + S_{cr}) p_{0,l} \quad (21)$$

172 Using the relationship $S_g + S_l + S_{cr} = 1$ and the definition of capillary pres-
 173 sure, equation 2, and defining the crystallization pressure p_x as the difference
 174 between the pressure of the crystal phase and the pressure of the liquid phase
 175 $p_x = p_{cr} - p_l$, equation 21 becomes:

$$p_s = p_g + (S_l + S_{cr}) p_c + S_{cr} p_x - S_g p_{0,g} - (S_l + S_{cr}) p_{0,l} \quad (22)$$

176 where $p_{0,l}$ is defined as:

$$p_{0,l} = \frac{1}{S_l + S_{cr}} \int_0^\infty \frac{2\sigma_{s,l}}{r} \frac{d(S_l + S_{cr})}{dr} dr \quad (23)$$

177 and $p_{0,g}$ as:

$$p_{0,g} = \frac{1}{S_g} \int_0^\infty \frac{2\sigma_{s,g}}{r} \frac{d(S_g)}{dr} dr = -\frac{1}{S_g} \int_0^\infty \frac{2\sigma_{s,g}}{r} \frac{d(S_l + S_{cr})}{dr} dr \quad (24)$$

178 Knowing that $\frac{2\sigma_{s,l}}{r} - \frac{2\sigma_{s,g}}{r}$ equals the capillary pressure p_c , we can write:

$$p_s = p_g + (S_l + S_{cr}) p_c + S_{cr} p_x - \int_0^\infty p_c \frac{d(S_l + S_{cr})}{dr} dr \quad (25)$$

Starting from a reference state $p_s = 0$ defined by $p_g = p_{atm}$, $p_c = p_{c,ref}$ and
 $p_x = p_{x,ref}$, and assuming that the gas pressure is constant and equal to the
 atmospheric pressure, equation 25 becomes:

$$p_s = \int_{p_{c,ref}}^{p_c} (S_l + S_{cr}) dp_c + S_{cr} (p_x - p_{x,ref}) \quad (26)$$

179 The effective stress tensor $\boldsymbol{\sigma}$ is given by:

$$\boldsymbol{\sigma} = \boldsymbol{D} (\boldsymbol{\epsilon} - \boldsymbol{\epsilon}_T) \quad (27)$$

180 where $\boldsymbol{D}$ is the 4th order elasticity tensor, assuming that the porous mate-
 181 rial exhibits linear elastic mechanical behavior. $\boldsymbol{\epsilon}$ is the second order strain
 182 tensor equal to the symmetric gradient of the displacement field $\mathbf{u}$ under the
 183 assumption of small deformations:

$$\boldsymbol{\epsilon} = \nabla^{sym} \mathbf{u} \quad (28)$$

184 $\boldsymbol{\epsilon}_T$ is the thermal strain tensor, accounting for the thermal expansion or
 185 contraction of the porous material:

$$\boldsymbol{\epsilon}_T = \alpha \mathbf{I} (T - T_{ref}) \quad (29)$$

186 with α the thermal expansion coefficient of the porous material and T_{ref} the
 187 reference temperature.

188 2.5. Damage

189 We assume that damage occurs, i.e. that a crack develops, when the
 190 j^{th} principal component σ_j of the effective stress tensor, determined from
 191 equation 16 using definitions 17 and 27, exceeds the material strength f_t^0 .
 192 This is expressed by the following criterion:

$$f = \sigma_j - f_t^0 \leq 0 \quad (30)$$

193 If equation 30 is violated at a material point, a crack surface develops normal
 194 to the j^{th} principal stress direction. The dependence of the material strength
 195 on the liquid saturation degree S_l is accounted for in the model (see equation
 196 38).

197 **3. Drying experiment, material and salt properties**

198 *3.1. Drying experiment*

199 Drying of a Savonnières limestone sample ($10 \times 10 \times 8.5 \text{ mm}^3$) at 45°C , ini-
200 tially saturated with a 5.8 molal sodium chloride solution, has been visualized
201 and quantified using quantitative neutron imaging analysis (Derluyn, 2012).
202 The moisture content resolution with this technique amounts to 0.04 kg/m^3 .
203 The sample was prepared by applying a water and vapor tight membrane
204 on the lateral sides (aluminum tape) in order to create a one-dimensional
205 drying process. Drying occurred in the direction perpendicular to the bed-
206 ding of Savonnières limestone. A hydrophobic treatment (SILRES BS 280,
207 Wacker) was applied on the upper 3 mm of the sample. Drying could only
208 occur through the hydrophobically treated upper part as the bottom sur-
209 face was sealed. The hydrophobic treatment was intended to prevent salt
210 efflorescence and induce in-pore crystallization. During the drying, the neu-
211 tron radiographs of high spatial resolution (nominal pixel size of $13.5 \text{ }\mu\text{m}$)
212 indicated considerable deformations after about 100 minutes. These defor-
213 mations are induced by crack formation due to the crystallization of sodium
214 chloride. The cracks resulting from the salt crystallization were character-
215 ized using X-ray micro-computed tomography. The experiment revealed that
216 the salt crystals precipitate in the upper region of the sample, mainly in the
217 hydrophobic zone, but below the top surface of the sample. Consequently,
218 cracks formed in this zone (see Figure 3).

219 3.2. Savonnières properties

220 The total open porosity Φ of the Savonnières limestone used for the ex-
 221 perimental study was determined by vacuum saturation and amounts 26.9%.
 222 The density of the limestone equals 1975 kg/m³. During capillary satura-
 223 tion, only 56% of the pore space gets filled, or the capillary active porosity of
 224 untreated Savonnières limestone amounts $\Phi_{unt} = 14.9\%$. The other pores are
 225 only active in the over-capillary regime (Carmeliet and Roels, 2002). When
 226 a hydrophobic treatment is applied, the treatment occupies a fraction of the
 227 pore space, defined by the porosity Φ_h . The capillary active pore space re-
 228 duces to $\Phi_{unt} - \Phi_h$. The porosity affected by the hydrophobic treatment, Φ_h ,
 229 at a certain position x is found by:

$$\Phi_h(x) = \Phi_{unt} - \frac{w_{l,cap}(x)}{\rho_l} \quad (31)$$

230 with $w_{l,cap}(x)$ the capillary moisture content at the position x , determined
 231 from the moisture profile in the capillary saturated sample in the absence
 232 of salt crystals. As soon as salt crystals start precipitating, they as well
 233 reduce the capillary active pore space. The crystals occupy a fraction of
 234 the pore space $\Phi_{cr} = \Phi S_{cr}$ and the capillary active pore space reduces to
 235 $\Phi_{unt} - \Phi_h - \Phi_{cr}$.

236 The moisture retention curve of untreated Savonnières limestone, describ-
 237 ing the liquid saturation degree $S_{l,unt}$ in function of capillary pressure, is
 238 approximated by a sum of power functions (van Genuchten, 1980; Durner,
 239 1994):

$$S_{l,unt}(p_c) = \sum_{j=1}^s l_j (1 + (c_j p_c)^{n_j})^{m_j} \quad (32)$$

240 with s the number of pore systems, l_j weight factors, and c_j , n_j and m_j model
 241 parameters. Parameter m_j can be estimated as (van Genuchten, 1980):

$$m_j = \frac{1 - n_j}{n_j} \quad (33)$$

242 For the wetting moisture retention curve in the capillary regime, the param-
 243 eters are given in Table 1. When the capillary active porosity is reduced
 244 by a hydrophobic treatment and/or the presence of salt crystals, the liquid
 245 saturation degree S_l is reduced in a simplified way by multiplying $S_{l,unt}$ with
 246 the factor $1 - \frac{\Phi_h}{\Phi_{unt}} - \frac{\Phi_{cr}}{\Phi_{unt}}$ (Derluyn, 2012).

247 The liquid permeability for pure water $K_{w,unt}$ of Savonnières limestone
 248 in function of capillary pressure was determined from the moisture profiles
 249 obtained by neutron imaging during a capillary uptake test, as explained in
 250 Derluyn et al. (2013). The liquid permeability for a salt solution $K_{l,unt}$ can
 251 be calculated from the liquid permeability of pure water as:

$$K_{l,unt} = K_{w,unt} \frac{\eta_w \rho_l}{\rho_w \eta_l} \quad (34)$$

252 where η is the viscosity. The viscosity of sodium chloride solutions with a
 253 concentration between 0 to 6 molal in a temperature range of 20 to 150°C is
 254 given in Kestin et al. (1981). The density, as function of temperature and
 255 concentration, can be calculated following Steiger (2000, 2008). The relation
 256 expressed by equation 34 was confirmed experimentally by Derluyn et al.
 257 (2013). When the capillary active pore space is reduced by a hydrophobic
 258 treatment and/or the presence of salt crystals, the liquid permeability K_l is
 259 reduced, similar to the liquid saturation degree, by multiplying $K_{l,unt}$ with
 260 the factor $1 - \frac{\Phi_h}{\Phi_{unt}} - \frac{\Phi_{cr}}{\Phi_{unt}}$ (Derluyn, 2012).

261 The vapor permeability δ_v was measured with the ‘cup method’ following
 262 EN ISO 12572:2001 (CEN, 2001). The nonlinear vapor permeability can be
 263 described in function of the vapor pressure p_v as:

$$\delta_v = \delta_{v,air} \cdot \left(a + b \exp \left(c \cdot \frac{p_v}{p_{v,sat}} \right) \right) \quad (35)$$

264 with a , b and c parameters. The vapor permeability in air $\delta_{v,air}$ is given by
 265 Schirmer’s equation (Schirmer, 1938; Ochs et al., 2008). For flow perpen-
 266 dicular to the bedding direction of the limestone, the parameters a , b and c
 267 amount 0.0109, 8.86×10^{-6} and 8.55, respectively.

268 The thermal conductivity λ was measured using the heat flow meter
 269 method (EN 1946-3:1999, SIA (1999)). An average thermal conductivity
 270 of 0.99 W/mK was found for dry Savonnières limestone. To incorporate the
 271 influence of moisture, the thermal conductivity of water λ_w , multiplied with
 272 the volume fraction of water, is added to the dry thermal conductivity:

$$\lambda(S_l) = \lambda_{dry} + \lambda_w \Phi S_l \quad (36)$$

273 Values for λ_w are given by Haynes and Lide (2012), e.g. at 20°C λ_w equals
 274 0.6 W/mK . The thermal capacity $c_{p,s}$ of Savonnières limestone is estimated
 275 to be 900 J/kgK (www.engineeringtoolbox.com). The thermal expansion
 276 coefficient α was determined by measuring the thermal dilation in a dynamic
 277 mechanical analyser (DMA 7e, Perkin Elmer) during a heating-cooling cycle
 278 (125°C - 25°C), an average value of 5.5 $\mu\text{m/mK}$ was obtained.

279 The E-modulus was measured on samples of 16 cm height and 4 x 4 cm²
 280 cross section. The samples were subjected to a compressive load up to 1/3rd
 281 of their compressive strength. During this compression the deformation was
 282 measured using a strain gauge, and the E-modulus was determined from

the load-deformation curve. In the dry state, an average E-modulus of 13.9 GPa is found perpendicular to the bedding direction. When the stone is capillary saturated, the E-modulus perpendicular to the bedding direction reduces to 11.2 GPa. The change of E-modulus with saturation degree can be approximated by:

$$E(S_l) = E_{wet} + (E_{dry} - E_{wet}) \exp\left(-p \frac{\Phi}{\Phi_{unt}} S_l\right) \quad (37)$$

with p a parameter, determined from experiments. We adopt a value of 36 (Poupeleer, 2007), but remark that this value was determined on calcium silicate board. The function in equation 37 expresses that the E-modulus decreases rapidly to the E-modulus of the wet state when the stone becomes wet ($S_l > 0$). The same behavior was, for example, observed by Van Den Abeele et al. (2002) on Meule sandstone.

The tensile strength of dry Savonnières limestone was determined from a tensile test. In the direction perpendicular to the bedding, the tensile strength $f_{t_{dry}}^0$ equals 1.8 MPa. The tensile strength of the bulk material in function of liquid saturation degree can be written as:

$$f_t^0(S_l) = \frac{f_{t_{dry}}^0}{E_{dry}} E(S_l) \quad (38)$$

assuming the same tensile strain in dry and wet conditions.

The Biot coefficient of Savonnières limestone was not measured experimentally, but estimated from literature data of a similar limestone (Lion et al., 2004). A value of 0.77 is assumed.

3.3. Sodium chloride properties

The sodium chloride diffusion coefficient in the porous material, $\mathbf{D}_i^l$, is defined by Buchwald (2000) as:

$$\mathbf{D}_i^l = \tau^{-1} D(C, T) \Phi S_l^n \quad (39)$$

where $D(C, T)$ is the diffusion coefficient in function of concentration and temperature in a non-dilute solution, taken from Rard and Miller (1979), τ is the tortuosity of the porous material, being 24.4 perpendicular to the bedding direction, and n is the saturation exponent, taken equal to 1.6 (Buchwald, 2000).

To estimate the heat of crystallization L_{cr} , the method described by Marliacy et al. (2000) is adopted, as described by Derluyn (2012). The heat capacity $c_{p,cr}$ of sodium chloride crystals is obtained from Haynes and Lide (2012).

The supersaturation U and the water activity a_w are calculated using the Pitzer ion interaction approach as described by Steiger et al. (2008), thus accounting for the non-ideal behavior of pore solutions. The supersaturation and the water activity are both function of the temperature and the salt concentration. The crystallization pressure p_x is then given by (Steiger, 2005a):

$$p_x = \frac{RT}{\bar{V}_{cr}} \ln U \quad (40)$$

with R the universal gas constant, T the absolute temperature and $\bar{V}_{cr}$ the molar volume of the crystal, being $27 \text{ cm}^3/\text{mole}$ for sodium chloride.

The kinetic growth parameters $K_{m,cr}$ and g_{cr} for sodium chloride equal $0.41 \text{ kg/m}^3\text{s}$ (Espinosa-Marzal, 2009) and 1, respectively.

324 4. Simulation results and discussion

325 In this section, we simulate the coupled heat-moisture-salt transport and
326 salt crystallization and predict the risk for salt damage for the experiment
327 described in section 3.1. Hence, we solve equations 1, 4, 5, 8 and 16 and
328 check when the damage criterion (equation 30) is violated. The equations are
329 solved using the finite element method to obtain the variation of the primary
330 variables p_c , C , T , S_{cr} and $\mathbf{u}$ in space and time. In order to obtain a mass and
331 energy conservative system of equations, a mixed form of the capacitive terms
332 is used, as described in Janssen et al. (2007). A staggered solution scheme
333 is used and each equation is solved implicitly using the Newton-Raphson
334 method. Numerical integration is performed by means of a Gauss-Lobatto
335 scheme. This has a similar accuracy as the more commonly used Gauss-
336 Legendre scheme, but suppresses oscillations in the solution field for our set
337 of highly non-linear PDE's.

338 4.1. Input, initial and boundary conditions

339 The physical properties of Savonnières limestone and sodium chloride
340 as given in sections 3.2 and 3.3 are used. The parameters v , l and U_{start}
341 in the U_{thr} -function (equation 13), which are related to the crystallization
342 kinetics, are the only parameters that cannot be determined from literature
343 or experiments. Therefore, the sensitivity of the results with respect to these
344 three parameters is assessed by conducting a parameter study. We perform
345 the simulation using an U_{start} -value of 1.5 or 2, a l -value of 1×10^{-4} or 1×10^{-3}
346 m and a v -value of $10 \frac{\Phi}{\Phi_{unt}}$, $100 \frac{\Phi}{\Phi_{unt}}$ or $1000 \frac{\Phi}{\Phi_{unt}}$, resulting in 12 different cases.
347 The U_{start} -value of 1.5 corresponds to a concentration increase of 9% by mass

348 with respect to the saturated concentration at 45°C (based on Steiger et al.
 349 (2008)). This value is close to the maximal value of 10% mentioned by Flatt
 350 (2002).

351 The simulation is performed on a 1-dimensional mesh of length L , where
 352 L equals the height of the sample used in the drying experiment, being 8.19
 353 mm. We acknowledge that the simulation does not completely represent
 354 the 3-dimensional nature of the sample. However, the drying process it-
 355 self, inducing the crystallization damage, can be considered to be mainly
 356 1-dimensional. As such, the crystallization and mechanical analysis can, in a
 357 first approximation, be regarded as 1-dimensional. The mesh consists of 100
 358 equidistant elements. The same time step is used for all discretized equa-
 359 tions. The time step is in the order of 1 to 5 ms, assuring convergence of the
 360 coupled system of equations.

361 The initial capillary pressure at time $t = 0$ equals -100 Pa for every
 362 position in the sample, corresponding to the capillary saturated state. The
 363 initial temperature of the sample is equal to 45°C. The initial concentration
 364 at every position in the sample equals 5.8 molal. In the initial state, no
 365 crystals are present in the sample.

The environment surrounding the sample during the experiment is char-
 acterized by a relative humidity RH_{env} of 5% and a temperature T_{env} of 45°C.
 Boundary conditions of the Neumann type are imposed on the top surface
 of the sample, being:

$$\bar{q}_m = CMT C(p_{v,env} - p_{v,surf}) \text{ with } p_{v,env} = p_{v,sat}(T_{env}) \cdot RH_{env} \quad (41)$$

$$\bar{q}_e = HTC(T_{env} - T_{surf}) + (c_{p,v}(T_{surf} - T_0) + L_v) \cdot \bar{q}_m \quad (42)$$

366 with $\bar{q}_m$ the moisture flux and $\bar{q}_e$ the heat flux at the boundary. $p_{v,surf}$ and

T_{surf} are the vapor pressure and the temperature at the boundary surface.
 The convective mass transfer coefficient $CMTC$ is determined based on in-
 verse modeling (Derluyn, 2012) and amounts 3.95×10^{-9} s/m. The convective
 heat transfer coefficient $CHTC$ is then given by the Chilton-Colburn analogy
 (Chilton and Colburn, 1934) and amounts 0.57 W/m²K. The radiative heat
 transfer coefficient $RHTC$ is 5.1 W/m²K (CEN, 2004) and the corresponding
 total heat transfer coefficient HTC is thus 5.67 W/m²K. Zero-flux boundary
 conditions are applied on the bottom side of the sample.

4.2. Results and discussion

From the experimental results, we know that the sample starts to deform
 considerably after 100 minutes, due to crack formation. We expect that
 the effective stress at a certain position in the sample exceeds the tensile
 strength around this time. With this assumption, we consider the material
 to mechanically behave homogeneously; and we remark that this approxi-
 mation does not explicitly account for the existence of local weak spots in
 the microstructure of the stone. An overview of the maximal effective stress
 reached after 2.5 hours of drying is given in Table 2 using different values
 for the parameters U_{start} , l and v . Only four of the twelve sets of parameters
 predict damage within the simulated time frame. The table indicates that
 the more crystals can spread within the sample (larger l value) and the faster
 the U_{thr} -function reduces to 1 (larger v value), the longer it takes before the
 effective stress exceeds the tensile strength.

We will further discuss three simulation results more in detail. We select
 the U_{start} -value of 1.5, which is the closest to the maximal value expected
 by Flatt (2002). We compare the simulation result using $l = 1 \times 10^{-4}$ and

392 $v = 100$, that results in damage after 114 minutes, with the simulation results
 393 using $l = 1 \times 10^{-4}$ and $v = 1000$ and using $l = 1 \times 10^{-3}$ and $v = 100$, which
 394 do not yield damage within the considered time period. The comparison is
 395 done for the first 114 minutes of the simulation. The parameter set with
 396 $l = 1 \times 10^{-4}$ and $v = 100$ gives the best agreement with the experimental
 397 result, whereas the other two parameter sets show the influence of different
 398 crystallization kinetics. The U_{start} -value of 1.5 is reached after 23 minutes.
 399 The effective stress and the strain evolution with time are given by the profiles
 400 in Figure 2. We observe that the highest stresses (Figure 2a) and strains
 401 (Figure 2d) develop at about 0.4 mm from the top of the sample. This is
 402 in agreement with the observed crack pattern in the sample. A vertical slice
 403 obtained from the X-ray tomographic dataset of the sample after the drying
 404 experiment is shown in Figure 3. A crack developed at the same position as
 405 where the effective stress reaches the tensile strength of 1.58 MPa.

406 The effective stresses in Figures 2a, 2b and 2c are directly related to
 407 the crystal saturation degree S_{cr} and the crystallization pressure p_x . It is
 408 the product of these two quantities that determines the effective stress, as
 409 expressed by equation 26. The profiles of S_{cr} and p_x are given in Figure
 410 4. In the simulation with $l = 1 \times 10^{-4}$ and $v = 100$, the highest amount
 411 of crystals is reached locally (Figure 4a), and the crystallization zone in
 412 the sample is small. When changing the v -value to 1000, the maximal S_{cr} -
 413 value reduces and the crystals are a little more spread (Figure 4b). When
 414 changing the l -value to 1×10^{-3} there is significantly more spreading of
 415 crystals, and the maximal S_{cr} -value consequently reduces further (Figure
 416 4c). The crystallization pressure is related to the concentration evolution,

417 given in Figures 5a, 5b and 5c. The concentration, and consequently the
 418 crystallization pressure, increase due to the drying process, and decrease due
 419 to the salt crystallization. The concentration in Figure 5b decreases faster
 420 in the crystallization zone than in Figure 5a due to the larger value for the
 421 parameter ν , and thus a faster decrease of the U_{thr} -value. The concentration
 422 in Figure 5c also decreases faster due to the larger parameter l , representing
 423 a larger influence length, and thus a larger crystallization zone. The moisture
 424 content profiles of the different simulations (Figures 5d, 5e and 5f) do not
 425 show a large difference. The difference is mainly in the upper part of the
 426 sample, where the crystals precipitate as indicated by the gray arrow in the
 427 figures.

As our sample can deform freely, the solid stress σ_s equals zero (i.e. is equal to the external mechanical stress). This means that the effective stress σ is only determined by the solid pressure p_s . Using equation 26 and considering that our simulation is 1-dimensional, so that we can denote the stresses by a scalar (i.e. we describe the stress along the height of the sample), gives:

$$\begin{aligned}
 \sigma &= b \left(\int_{-100}^{p_c} (S_l + S_{cr}) dp_c + S_{cr} p_x \right) \\
 &= b \left(\int_{-100}^{p_c} \left(S_{l,unt} \left(1 - \frac{\Phi_h}{\Phi_{unt}} \right) \right) dp_c + S_{cr} p_x \right)
 \end{aligned} \tag{43}$$

428 The effect of the hygric stresses, expressed by the first term in equation 43
 429 is found to be negligible in this simulation, as they only range in the order
 430 of magnitude of 1000 Pa. Thus the effective stress, given in Figures 2a, 2b,
 431 2c is approximately given by:

$$\sigma \approx b S_{cr} p_x \tag{44}$$

432 The strains in Figures 2d, 2e and 2f are related to the crystal formation
433 and to the temperature change in the sample. The sample cools down due
434 to evaporative cooling as represented for the boundary location, $x = L$, in
435 Figure 6. At other positions in the sample, the temperature evolution is
436 similar. The cooling causes a shrinkage of the sample. As the sample can
437 deform freely and the cooling is uniform over the sample, the strains due to
438 the cooling are uniform and no internal stresses develop due to the thermal
439 shrinkage. When crystals start to form, they cause expansion of the sample
440 in the zone where the crystals precipitate.

441 The liquid weight decrease is given in Figure 7a. The three simulations
442 approach the experimentally obtained data. The accumulated crystal mass is
443 given in Figure 7b. An important observation is that the case where damage
444 is induced after 114 minutes (simulation 1 with $l = 1 \times 10^{-4}$ and $v = 100$)
445 corresponds to the case where the lowest amount of accumulated crystal mass
446 is found. This indicates that the risk for salt damage depends strongly on
447 the crystallization kinetics, rather than on the amount of crystals formed.
448 The parameter study indicates that when it is more difficult for the crystals
449 to form (the lower l and the lower v), the damage will occur faster once
450 crystals start to grow. This is because higher crystallization pressures can
451 build up and the crystals precipitate more localized, causing higher effective
452 stresses locally. This result shows the importance of the nucleation and
453 growth kinetics for the correct prediction of salt damage risks. It indicates
454 that if you can control the kinetics of crystallization, you can control salt
455 damage.

456 5. Conclusions

457 We have developed a fully coupled computational model that describes
458 heat, water and ion transport, salt crystallization and deformations and dam-
459 age induced by hygro-thermal and crystallization stresses. The model pre-
460 dictes the macroscopic behavior and physical degradation of porous materials.
461 The model has been discussed with the focus on the prediction of salt damage
462 caused by the formation of sodium chloride crystals in a porous limestone
463 during drying. The simulation results show a good agreement with exper-
464 imental data, obtained from neutron and X-ray imaging techniques, when
465 choosing suitable parameters for the crystallization kinetics. These param-
466 eters are estimated based on a sensitivity study. The simulations show that
467 the effective stresses resulting from salt crystallization do not only depend on
468 the crystallization pressure, which is related to the supersaturation, but also
469 on the amount of salt crystals forming and the localization of these crystals.
470 In order to include the last aspect, a non-local formulation was incorporated
471 in the model. Future research could focus on experimental and/or model-
472 ing studies for the reliable prediction of the kinetic parameters. The results
473 presented in this paper suggest that controlling the nucleation and growth
474 kinetics is the key factor to control crystallization damage in porous building
475 materials.

476 6. Acknowledgments

477 The Department of Architecture at ETH Zurich is acknowledged for co-
478 funding the research of Hannelore Derluyn.

479 7. Vitae

480 7.1. *Dr. ir. Hannelore Derluyn*

481 Hannelore Derluyn received her master degree in civil engineering from
482 K.U. Leuven (Belgium) in July 2006, magna cum laude. Subsequently, she
483 was a research affiliate at K.U. Leuven. She started her PhD studies there
484 in January 2008 and pursued her research at ETH Zurich (Switzerland).
485 She obtained her PhD degree from ETH Zurich in November 2012 and was
486 awarded the ETH Medal. During her PhD studies, she was an academic guest
487 at EMPA Dübendorf (Switzerland), Princeton University (USA) and Ghent
488 University (Belgium). She was a postdoc at ETH Zurich/EMPA Dübendorf.
489 From October 2013, she is an FWO-postdoc fellow at Ghent University.

490 7.2. *Dr. ir. Peter Moonen*

491 Peter Moonen studied civil engineering at K.U. Leuven (Belgium), and
492 graduated in July 2003 with summa cum laude. After graduation, he started
493 working on an interdisciplinary project, which resulted in a dual PhD degree,
494 issued by both the K.U. Leuven and the Delft University of Technology (The
495 Netherlands). In 2009-2010, he had the opportunity to do a postdoc at
496 the ETH Zurich (Switzerland). Since the beginning of 2011, he is research
497 scientist at Empa Dübendorf (Switzerland) and lecturer at ETH Zurich.

498 7.3. *Prof. dr. ir. Jan Carmeliet*

499 Since June 2008, Jan Carmeliet is full professor at the Chair of Building
500 Physics at ETH Zurich and head of the Laboratory of Building Science and
501 Technology of EMPA Dübendorf (Switzerland). Jan Carmeliet received his

502 PhD in Civil Engineering at K.U. Leuven (Belgium) in 1992 and was a post-
503 doctoral fellow at the Delft University of Technology (The Netherlands). He
504 has been Assistant (1998), Associate (2001) and Full Professor (2004) at K.U.
505 Leuven and part-time Professor at the Eindhoven University of Technology
506 (since 2001). In 2007 he was on sabbatical leave at the University of Illinois
507 at Urbana Champaign and at Los Alamos Governmental Laboratories.

508 **References**

509 Buchwald, A., 2000. Determination of the ion diffusion coefficient in mois-
510 ture and salt loaded masonry materials by impedance spectroscopy, in:
511 3rd International PhD Symposium, Vol. 2., 10-13 October 2000, Vienna,
512 Austria, pp. 475–482.

513 Carmeliet, J., Roels, S., 2002. Determination of the Moisture Capacity of
514 Porous Building Materials. *J. Build. Phys.* 25 (3), 209–237.

515 CEN, 2001. EN ISO 12572:2001 Hygrothermal performance of building ma-
516 terials and products - Determination of water vapour transmission prop-
517 erties.

518 CEN, 2004. prEN 15026 Hygrothermal performance of building components
519 and building elements - Assessment of moisture transfer by numerical sim-
520 ulation.

521 Chilton, T., Colburn, A. P., 1934. Mass transfer (absorption) coefficients.
522 Prediction from data on heat transfer and fluid friction. *Ind. Eng. Chem.*
523 26 (11), 1183–1187.

- 524 Coussy, O., 2004. Poromechanics, John Wiley & Sons Ltd., Chichester, UK.
- 525 Coussy, O., 2006. Deformation and stress from in-pore drying-induced crys-
526 tallization of salt. *J. Mech. Phys. Solids* 54 (8), 1517–1547.
- 527 Coussy, O., 2010. Mechanics and Physics of Porous Solids, first ed. John
528 Wiley & Sons Ltd., Chichester, UK.
- 529 Derluyn, H., 2012. Salt transport and crystallization in porous limestone:
530 neutron - X-ray imaging and poromechanical modeling, Diss. ETH No.
531 20673. Ph.D. thesis, ETH Zurich, Switzerland.
- 532 Derluyn, H., Griffa, M., Mannes, D., Jerjen, I., Dewanckele, J., Vontobel, P.,
533 Sheppard, A., Derome, D., Cnudde, V., Lehmann, E., Carmeliet, J., 2013.
534 Characterizing saline uptake and salt crystal distributions in porous lime-
535 stone with neutron radiography and X-ray micro-tomography. *J. Build.*
536 *Phys.* 36 (4), 353–374.
- 537 Durner, W., 1994. Hydraulic conductivity estimation for soils with heteroge-
538 neous pore structure. *Water Resour. Res.* 30 (2), 211–223.
- 539 Espinosa, R. M., Franke, L., Deckelmann, G., Gunstmann, C., 2007. Gekop-
540 pelter Wärme- und Stofftransport einschließlich der Korrosionsprozesse
541 in porösen Baustoffen mit dem Simulationsprogramm AStra. *Bauphysik*
542 29 (3), 187–193.
- 543 Espinosa, R. M., Franke, L., Deckelmann, G., 2008. Phase changes of salts
544 in porous materials: Crystallization, hydration and deliquescence. *Constr.*
545 *Build. Mater.* 22 (8), 1758–1773.

- 546 Espinosa-Marzal, R. M., 2009. Personal communication.
- 547 Flatt, R. J., 2002. Salt damage in porous materials: how high supersatura-
548 tions are generated. *J. Cryst. Growth* 242 (3-4), 435–454.
- 549 Haynes, W., Lide, D. (Eds.), 2012. *CRC Handbook of Chemistry and Physics*,
550 92nd ed. Internet Version 2012.
- 551 Janssen, H., 2002. The influence of soil moisture transfer on building heat
552 loss via the ground. Ph.D. thesis, K.U. Leuven, Belgium.
- 553 Janssen, H., Blocken, B., Carmeliet, J., 2007. Conservative modelling of
554 the moisture and heat transfer in building components under atmospheric
555 excitation. *Int. J. Heat Mass Tran.* 50 (5-6), 1128–1140.
- 556 Kestin, J., Ezzat Khalifa, H., Correia, R. J., 1981. Tables of the dynamic and
557 kinematic viscosity of aqueous NaCl solutions in the temperature range 20-
558 150°C and the pressure range 0.1-35 MPa. *J. Phys. Chem. Ref. Data* 10 (1),
559 71–87.
- 560 Koniorczyk, M., 2010. Modelling the phase change of salt dissolved in pore
561 water - Equilibrium and non-equilibrium approach. *Constr. Build. Mater.*
562 24 (7), 1119–1128.
- 563 Koniorczyk, M., 2012. Salt transport and crystallization in non-isothermal,
564 partially saturated porous materials considering ions interaction model.
565 *Int. J. Heat Mass Tran.* 55 (4), 665–679.
- 566 Lion, M., Skoczylas, F., Ledésert, B., 2004. Determination of the main hy-

567 draulic and poro-elastic properties of a limestone from Bourgogne, France.
568 Int. J. Rock Mech. Min. 41 (6), 915–925.

569 Marliacy, P., Solimando, R., Bouroukba, M., Schuffenecker, L., 2000. Ther-
570 modynamics of crystallization of sodium sulfate decahydrate in H₂O-NaCl-
571 Na₂SO₄: application to Na₂SO₄·10H₂O-based latent heat storage materi-
572 als. Thermochim. Acta 344, 85–94.

573 Moonen, P., Sluys, L. J., Carmeliet, J., 2010. A continuous-discontinuous
574 approach to simulate physical degradation processes in porous media. Int.
575 J. Numer. Meth. Eng. 84, 1009–1037.

576 Moonen, P., Sluys, L. J., Carmeliet, J., 2011. A continuous-discontinuous
577 approach to simulate heat transfer in fractured media. Transport Porous
578 Med. 89 (3), 399–419.

579 Nicolai, A., Grunewald, J., Zhang, J. S., 2007. Salztransport und
580 Phasenumwandlung - Modellierung und numerische Lösung im Simula-
581 tionsprogramm Delphin 5. Bauphysik 29 (3), 231–239.

582 Ochs, F., Heidemann, W., Mullersteinhagen, H., 2008. Effective thermal con-
583 ductivity of moistened insulation materials as a function of temperature.
584 Int. J. Heat Mass Tran. 51 (3-4), 539–552.

585 Poupeleer, A., 2007. Transport and crystallization of dissolved salts in
586 cracked porous building materials. Ph.D. thesis, K.U. Leuven, Belgium.

587 Rard, J. A., Miller, D. G., 1979. The mutual diffusion coefficients of NaCl-
588 H₂O and CaCl₂-H₂O at 25°C from Rayleigh interferometry. J. Solution
589 Chem. 8 (10), 701–716.

- 590 Scherer, G. W., 1999. Crystallization in pores. *Cement Concrete Comp.* 29,
591 1347–1358.
- 592 Scherer, G. W., 2004. Stress from crystallization of salt. *Cement Concrete*
593 *Res.* 34, 1613–1624.
- 594 Schirmer, R., 1938. Die Diffusionszahl von Wasserdampf-Luftgemischen und
595 die Verdampfungs-geschwindigkeit. *ZVDI Beheft Verfahrenstechnik* 6,
596 170.
- 597 SIA, 1999. EN 1946-3:1999 Wärmetechnisches Verhalten von Baupro-
598 dukten und Bauteilen - Technische Kriterien zur Begutach-
599 tung von Laboratorien bei der Durchführung der Messungen von
600 Wärmeübertragungseigenschaften - Teil 3: Messung nach dem Verfahren
601 mit dem Wärmestrom.
- 602 Steiger, M., 2000. Chapter 6: Total volumes of crystalline solids and salt
603 solutions, in: Price, C. (Ed.), *An expert chemical model for determining*
604 *the environmental conditions needed to prevent salt damage in porous*
605 *materials*, pp. 53–63.
- 606 Steiger, M., 2005a. Crystal growth in porous materials - I: The crystallization
607 pressure of large crystals. *J. Cryst. Growth* 282 (3-4), 455–469.
- 608 Steiger, M., 2005b. Crystal growth in porous materials - II: Influence of
609 crystal size on the crystallization pressure. *J. Cryst. Growth* 282 (3-4),
610 470–481.
- 611 Steiger, M., 2008. Personal communication.

- 612 Steiger, M., Kiekbusch, J., Nicolai, A., 2008. An improved model incorpo-
613 rating Pitzer's equations for calculation of thermodynamic properties of
614 pore solutions implemented into an efficient program code. *Constr. Build.*
615 *Mater.* 22 (8), 1841–1850.
- 616 Van Den Abeele, K. E.-A., Carmeliet, J., Johnson, P. A., Zinszner, B., 2002.
617 Influence of water saturation on the nonlinear elastic mesoscopic response
618 in Earth materials and the implications to the mechanism of nonlinearity.
619 *J. Geophys. Res.* 107, 2121.
- 620 van Genuchten, M. T., 1980. A closed-form equation for predicting the hy-
621 draulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 892–898.

Figure 1: Schematic illustration of a crystal in a pore. A liquid film is maintained between the crystal surface and the pore wall.

Table 1: Parameters for the analytical fit of the capillary water retention curve.

i	1	2	3
c_i	8.0×10^{-7}	7.0×10^{-6}	1.3×10^{-4}
n_i	4.27	1.98	1.85
l_i	0.135	0.256	0.165

Table 2: Maximal principal effective stress $\sigma_{I,max}$ after 2.5 hours using different parameter values, the height at which this effective stress is reached in the sample, and the time at which cracking occurs if the principal effective stress exceeds the tensile strength. The ‘-’ symbol indicates that no cracks formed during the first 2.5 hours. The simulations indicated in bold are discussed further in detail.

U_{start}	l m	ν	$\sigma_{I,max}$ MPa	height mm	time to crack min.
1.5	1×10^{-3}	10	1.03	7.78	-
1.5	1×10^{-3}	100	0.42	7.86	-
1.5	1×10^{-3}	1000	0.41	7.86	-
1.5	1×10^{-4}	10	$> f_t^0$	7.86	89
1.5	1×10^{-4}	100	$> f_t^0$	7.78	114
1.5	1×10^{-4}	1000	1.06	7.62	-
2.0	1×10^{-3}	10	1.48	7.86	-
2.0	1×10^{-3}	100	0.31	7.86	-
2.0	1×10^{-3}	1000	0.28	7.86	-
2.0	1×10^{-4}	10	$> f_t^0$	7.86	113
2.0	1×10^{-4}	100	$> f_t^0$	7.86	115
2.0	1×10^{-4}	1000	0.95	7.62	-

Figure 2: Effective stress (a-b-c) and strain (d-e-f) over the height of the sample for different model parameters: (a)&(d) $l = 10^{-4}$, $v = 100$, (b)&(e) $l = 10^{-4}$, $v = 1000$, (c)&(f) $l = 10^{-3}$, $v = 100$. Crystallization starts after 23 minutes.

Figure 3: Comparison between the effective stress evolution, simulated with $l = 10^{-4}$, $\nu = 100$ (Figure 2a) and the crack pattern in the sample visualized with X-ray micro-tomography. A crack is observed at the position where the maximal effective stress develops in the simulation.

Figure 4: Salt crystallization degree (a-b-c) and crystallization pressure (d-e-f) over the height of the sample with different model parameters: (a)&(d) $l = 10^{-4}$, $v = 100$, (b)&(e) $l = 10^{-4}$, $v = 1000$, (c)&(f) $l = 10^{-3}$, $v = 100$. Crystallization starts after 23 minutes.

Figure 5: Salt concentration (a-b-c) and moisture content (d-e-f) over the height of the sample with different model parameters: (a)&(d) $l = 10^{-4}$, $v = 100$, (b)&(e) $l = 10^{-4}$, $v = 1000$, (c)&(f) $l = 10^{-3}$, $v = 100$. Crystallization starts after 23 minutes. The gray arrows in figures d-e-f indicate where the main difference in the moisture profiles can be observed.

Figure 6: Temperature evolution at the boundary $x = L$ during drying. At other locations in the sample, the temperature evolution is similar.

Figure 7: (a) Weight decrease and (b) salt accumulation in the sample using different model parameters for nucleation: (1) $l = 10^{-4}$, $v = 100$, (2) $l = 10^{-4}$, $v = 1000$, (3) $l = 10^{-3}$, $v = 100$.