

## **Numerical simulation of gypsum transport and crystallization**

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### **Abstract**

Over the last few decades, brick masonry buildings in the UK, The Netherlands and Belgium have started suffering from a new type of salt efflorescence. This new efflorescence consists of sparingly soluble gypsum, and is therefore strongly persistent. Although gypsum efflorescence has already been known for several decades, there are still many open questions regarding the mechanisms behind this phenomenon. Numerical simulation of the transport and crystallization of gypsum in porous materials can contribute to a better understanding of the underlying processes, hence being helpful in the search for causes and solutions. However, due to the low solubility of gypsum and insensitivity to changes in temperature and relative humidity, calcium sulphate is generally not included in simulation software for salt transport and crystallization in porous materials. Therefore, this paper focuses on the numerical implementation of gypsum transport and crystallization in the Delphin simulation environment. As initial application, the simulation of wicking test is performed. The uptake test comprises an initially dry material sample in contact with gypsum solution at the bottom surface, while evaporation is allowed only at the top surface. The main objective is the study of the processes of transport and crystallization of gypsum in porous media, with relation to gypsum efflorescence on brick masonry.

**Keywords:** gypsum efflorescence, numerical simulation, transport and crystallization, gypsum solution uptake test.

## **1 Introduction**

Gypsum efflorescence is an aesthetical problem of masonry facades which has started appearing in the UK, The Netherlands and also in Belgium over the last few decades. It is a form of persistent white-grey discoloration, mainly developing on walls which are highly exposed to wind-driven rain [1–3]. This new type of efflorescence brought a growing number of complaints to the Belgium brick industry, which motivated a field survey and case study in Belgium [3]. After investigating 28 cases it was concluded that the efflorescence is composed of relatively insoluble gypsum and that it solely affects buildings which were erected over the last twenty years. The facades oriented towards South and West showed to be most affected. According to the building owners, the efflorescence started to develop several years after the construction, making it unclear whether it is a slow or delayed process. The relevant brick types were identified, but no connection between gypsum efflorescence and brick properties - moisture transfer properties and calcium sulphate content specifically - was found.

Despite the fact that this phenomenon has been known for several years already, the exact mechanisms and reasons for its appearance remain unknown. Therefore a numerical simulation of the transport and crystallization of gypsum in porous materials can contribute to a better understanding of the underlying processes, and hence help in the search for causes and solutions. Although there are several works that deal with the numerical modelling of salt transport and crystallization in porous materials [4, 5], neither of them includes gypsum or any other form of calcium sulphate. Its low solubility, insensitivity to changes in relative humidity and temperature, and the different mechanisms of causing damage, are all the reasons why it is excluded from numerical models [6]. However, to simulate gypsum transport and crystallization in the building materials, the same parameters and properties as for any other salt and salt solution are required. This includes the basic physical and chemical properties of gypsum and its solution, such as the density, solubility, heat capacity, viscosity, surface tension and heat of dissolution. The diffusion coefficient and activation energy are required for the simulation of transport, while the kinetic parameters for crystallization and dissolution are necessary for description of phase transitions [4, 5]. All these properties are equivalent to those of free salt solutions. Their connection and relation with the salts in porous building materials are not going to be the focus of this work, as they are detailed explained elsewhere [4, 5].

Therefore, the objective of this paper is to gather and implement all the parameters of calcium sulphate dihydrate and its solution, necessary for simulation of gypsum transport and crystallization in the Delphin simulation environment. Furthermore, the model application is illustrated via the simulation of gypsum solution wicking experiment. The test comprises an initially dry sample in contact with gypsum solution at the bottom face, while evaporation is allowed only at the top face. These

simulations make up the first step towards a better insight into how gypsum is transported, where it crystallizes and which parameters and properties are of a great importance for numerical modelling of calcium sulphate transport. Additionally the limitations of the model and needs for further research are discussed.

## 2 Parameterization of calcium sulphate

### 2.1 Molality based numerical model

Even though tabulated values of many electrolyte solution properties are available in the literature, most of them are only valid within limited ranges of temperature and concentration. Therefore, the molality based Pitzer ion interaction approach is used to predict many of the desired binary and salt mixture solution properties in the Delphin program. This well-known model is used in the area of electrolyte chemistry as well as geology. Developed by Kenneth S. Pitzer, it represents a system of equations which describe the thermodynamic properties of mixed and pure electrolyte solutions, within an experimental accuracy. The main objective of such a model is to reproduce the properties of solutions by using simple mathematical equations for pure electrolyte solutions as well as for mixed solutions. These equations require only a few parameters, which are obtained from experimental data and mainly tabulated in the work of Pitzer [7].

### 2.2 Basic properties of gypsum and gypsum solution

This part of the paper deals with the description and calculation of the basic physical and chemical properties of gypsum and gypsum solution. Firstly, ion and water activities, depending on temperature and concentration, are determined in order to calculate the density and solubility. Secondly, the viscosity, surface tension, heat capacity and heat of dissolution are discussed.

#### 2.2.1 Ion activity

One of the most important parameters in the thermodynamic calculations is the ion activity. It describes the effective concentration of chemical substances in the solution. For ideal solutions, the activity of an ion equals its concentration. However, an increase of concentration results in a deviation from ideal solutions, which is described by the activity coefficient  $\gamma$ . General equations for the calculation of the ion activity and the activity coefficients are available in the paper of Pitzer [7], while the calculation for pure calcium sulphate solution is given by the following equations:

$$\ln a_i = \ln \gamma_i + \ln m_i \quad (1)$$

$$\ln \gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + zC_{Ma}) + z_M \sum_c \sum_a m_c m_a C_{ca} \quad (2)$$

$$\ln \gamma_X = z_X^2 F + \sum_a m_c (2B_{cX} + ZC_{cX}) + |z_X| \sum_c \sum_a m_c m_a C_{ca} \quad (3)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{\frac{1}{2}}) + \beta_{MX}^{(2)} g(\alpha_2 I^{\frac{1}{2}}) \quad (4)$$

$$g(x) = 2[1 - (1+x)e^{-x}] / x^2 \quad (5)$$

$$F = -A_\Phi \left[ \frac{1}{(1+bl^2)} + \frac{2}{b} \ln(1+bl^2) \right] + m_c m_a B'_{ca} \quad (6)$$

$$B'_{MX} = \frac{1}{I} \left[ \beta_{MX}^{(1)} g'(\alpha_1 I^{\frac{1}{2}}) + \beta_{MX}^{(2)} g'(\alpha_2 I^{\frac{1}{2}}) \right] \quad (7)$$

$$g'(x) = \frac{-2}{x^2} [1 - (1+x + \frac{x^2}{2})e^{-x}] \quad (8)$$

where  $a_i$  is the ion activity [-],  $m_i$  is the molality of ion species [mol/kg],  $\gamma_M$  and  $\gamma_X$  are the activity coefficients [-] of the cation  $C_a^{2+}$  and the anion  $SO_4^{2-}$  respectively. The subscripts c and a refer to anions and cations present in a solution.  $B_{MX}$  and  $C_{MX}$  are the second and the third virial coefficients [-];  $I$  is the ionic strength [mol/kg] and  $Z$  is the charge density [mol/kg];  $b$  is the constant  $1.2 \text{ kg}^{0.5}/\text{mol}^{0.5}$ .  $A_\Phi$  is the Debye-Hückel parameter for the osmotic coefficient [ $\text{kg}^{0.5}/\text{mol}^{0.5}$ ], whose temperature dependence is described by equation (9) [8]:

$$A_\Phi(T) = -0.817653 - \frac{0.8685276}{T - 222K} + \frac{19251}{T^2} + 5.251484 \cdot 10^{-3}T + 9.338559 \cdot 10^{-12}T^4 \quad (9)$$

In the expression for the second virial coefficient,  $\beta^{(i)}$  are adjustable binary interaction parameters. Parameters  $\alpha_i$  are constants which have values of  $\alpha_1 = 2.0$  and  $\alpha_2 = 0$  for all electrolytes, except for 2-2 type salts, like calcium sulphate [7]. According to Pitzer and Mayorga [9], 2-2 electrolytes tend to form ion pairs, due to electrostatic forces. Nevertheless, considering ion pairs as separate species would make the calculations much more complex. The solution was found by adding the  $\beta^{(2)}$  term in the expression for the second virial coefficient and setting the values of  $\alpha$  to  $\alpha_1 = 1.4 \text{ kg}^{0.5}/\text{mol}^{0.5}$  and  $\alpha_2 = 12 \text{ kg}^{0.5}/\text{mol}^{0.5}$ . Although Pitzer [7] provides binary interaction parameters for calcium sulphate, with values of 0.2, 3.1973 and -54.24 for  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $\beta^{(2)}$  respectively, they are constant and thus independent of temperature. In the work of Steiger et al. [8] the

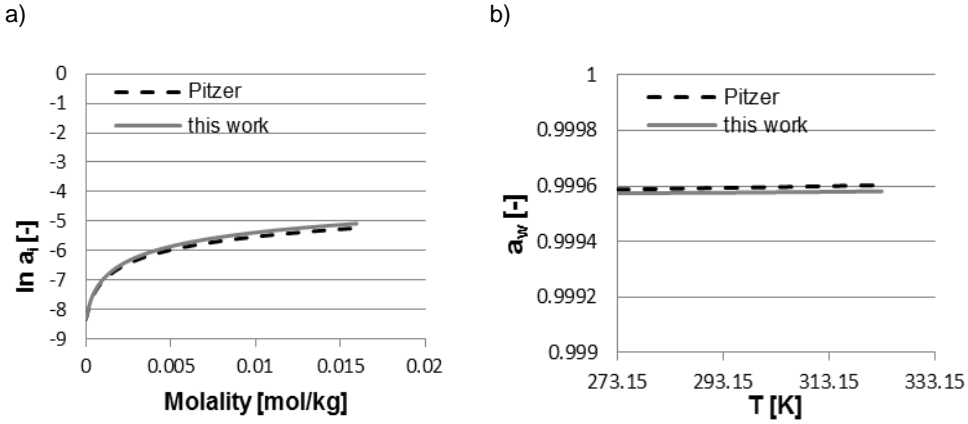
temperature dependence of all interaction parameters of different salts is described with the following function:

$$P(T) = q_1 + q_2 \left( \frac{1}{T} - \frac{1}{T_R} \right) + q_3 \ln \left( \frac{T}{T_R} \right) + q_4 (T - T_R) + q_5 (T^2 - T_R^2) + q_6 \ln(T - 225) \quad (10)$$

where  $T_R = 298.15\text{K}$  is a reference temperature and  $q_i$  are tabulated values for many salts. This improved model and parameterization of Steiger et al. [8] was implemented and used in Delphin. However, the parameterization of the temperature dependence of calcium sulphate is not provided. Møller [10] studied the prediction of mineral solubilities in natural waters, for the system of Na-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O. In her work, the temperature dependence of binary interaction parameters,  $\beta^{(i)}$  and  $C^\Phi$ , is described with equation ( 11):

$$f(T) = a_1 + a_2 T + \frac{a_3}{T} + a_4 \ln T + \frac{a_5}{T-263} + a_6 T^2 + \frac{a_7}{680-T} + \frac{a_8}{T-227} \quad (11)$$

For calcium sulphate,  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\Phi$  are set as constants with values of 0.15, 3.0 and 0 respectively, with following fitting parameters:  $a_1 = -129.399287$  and  $a_2 = 0.400431027$ , while the rest is equal to 0. Since the temperature dependence of interaction parameters in Delphin is described by equation ( 10) [4], the constants for calcium sulphate from equation ( 11) are fitted to function ( 10). The constant values for  $\beta^{(0)}_{\text{CaSO}_4}$ ,  $\beta^{(1)}_{\text{CaSO}_4}$  and  $C^\Phi_{\text{CaSO}_4}$  are kept the same, while for the  $\beta^{(2)}_{\text{CaSO}_4}$  values of  $q_1 = -10.01077629995$  and  $q_4 = 0.400431027$  are obtained and the rest is equal to zero. The obtained parameters for calcium sulphate are valid for temperatures from 0 to 50°C [10], which is acceptable for the scope of this work. Although the difference between  $\beta^{(2)}$  suggested by Pitzer and the one from Møller seems large, based on the calculated ion activity at a reference temperature of 25°C, this difference seems to be negligible (see Figure 1a). Even though it would be possible to use Pitzer's constant values of  $\beta^{(i)}$  for the present work, we proceed with the suggestion of Møller; this leaves us the possibility to include interactions with other ions, where the influence of temperature can be significant. In addition, the model of Møller is generally valid for higher levels of concentration [10].



**Figure 1:** a) Activity of ions in function of molality at 298.15K; b) water activity in function of temperature, at saturation level

### 2.2.2 Water activity

As the vapour diffusion inside the porous materials is influenced by the moisture saturation level as well as the salt content, the water activity is a quantity which describes the reduction of vapour pressure over the salt solution inside unsaturated porous media [4]. It is also necessary for the calculation of the equilibrium constant and thus the saturation ratio, which is essential for determining whether crystallization or dissolution will occur. Therefore, the calculation of this property is one of the advantages of the Pitzer ion interaction approach. The water activity is described by the following equation:

$$\ln a_w = -\phi M_w \sum_i m_i \quad (12)$$

where  $\phi$  is the osmotic coefficient [-],  $M_w$  is the molar mass of water [kg/mol] and  $m_i$  is the molality of dissolved ions. The general equation for the osmotic coefficient is presented in the work of Pitzer [7], while the reduced one, for the pure solution of calcium sulphate is given by the equation (13):

$$(\phi - 1) = \frac{2}{\sum_i m_i} \left[ \frac{-A_\phi I^{\frac{3}{2}}}{(1 + bI^{\frac{1}{2}})} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \right] \quad (13)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 I^{1/2}} + \beta_{MX}^{(2)} e^{-\alpha_2 I^{1/2}} \quad (14)$$

Fitting parameters for the virial coefficients,  $B_{MX}^\phi$  and  $C_{MX}$ , are the same as for the ion activities. As the solubility of gypsum is only 0.015 mol/kg of water at room temperature [11], the influence of dissolved calcium and sulphate ions on the water activity is almost negligible. For the temperature range from 0 to 50°C, the water activity does not differ much from unity (see Figure 1b), which also confirms that gypsum is insensitive to the changes in the temperature.

### 2.2.3 Density of solution

Although, the tabulated values of densities for different electrolyte solutions are available in the literature, they are often valid for limited ranges of temperature and concentration. Therefore the Pitzer ion interaction model can be used for the calculation of densities for salt mixtures as well as for binary solutions [4]. The density of a solution, containing 1kg of water, can be calculated by equation (15):

$$\rho_{sol} = \frac{1\text{kg} + \sum_i m_i M_i}{\frac{1\text{kg}}{\rho_w} + \sum_i m_i V_i^0 + V_{mix}^{ex}} \quad (15)$$

where  $m_i$  and  $M_i$  are the molality and molar mass of ions, respectively.  $V_w^0$  and  $V_i^0$  are the molar volume of water and the partial molar volumes of the ions, while  $\rho_w$  is water density.  $V_{mix}^{ex}$  is the excess molar volume, which is the result of the interaction between ions and water. The temperature dependence of the partial molar volumes  $V_i^0$  is described by equation (16):

$$f(T) = a_0 + a_1 \left( \frac{1}{T-225} \right) + a_2 \frac{1}{T} + a_3 T + a_4 T^2 + a_5 \ln T \quad (16)$$

The fitting parameters  $a_i$  for calcium and sulphate ions are listed in Table 1 [8].

**Table 1:** Fitting parameters for the partial molar volumes of calcium and sulphate ions

	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$
Ca	4.79700693	-429.486853	0	-0.0568315647	0	0
SO <sub>4</sub>	409.4060315	-618.1208309	-56791.12672	-0.65897533	0	0

The calculated values of the partial molar volumes for calcium and sulphate ions at the reference temperature of 298.15K are -18.0186 and 14.0 cm<sup>3</sup>/mol respectively, which is in a good agreement with the values  $V_{Ca} = -18.4\text{cm}^3/\text{mol}$  and  $V_{SO_4} = 13.98\text{cm}^3/\text{mol}$  reported in the work of Konstantinos and Georg [12]. The Pitzer ion interaction approach plays the role in the calculation of the excess molar volume (equation (17)).

$$V_{\text{mix}}^{\text{ex}} = A_v \frac{1}{b} \ln(1+b\sqrt{I}) + RT \left[ \sum_c \sum_a m_c m_a (2B_{ca}^V + ZC_{ca}^V) \right] \quad (17)$$

$$B_{\text{MX}}^V = \beta_{\text{MX}}^{(0)V} + \beta_{\text{MX}}^{(1)V} g(\alpha_1 |z|) + \beta_{\text{MX}}^{(2)V} g(\alpha_2 |z|) \quad (18)$$

Although,  $\beta^{(i)V}$  and  $C_{ca}^V$  are also expressed with the function ( 16 ), due to the low solubility of calcium sulphate, these parameters can be neglected in the calculation of  $V_{\text{mix}}^{\text{ex}}$  [13]. Nicolai [4] obtained a similar observation: for low concentration solutions, the influence of excess volume is negligible, while in the case of high ionic strengths, ion interaction can significantly influence the solution volume. Since the values for  $\beta^{(i)V}$  and  $C_{ca}^V$  are not established for the present work, the calculation of the solution density was executed in two ways. The first one excluded the excess molar volume completely, while the other included  $V_{\text{mix}}^{\text{ex}}$ , which is calculated taking into account only the first term of equation ( 17 ). Due to the very low solubility of gypsum, the solution density is only slightly different from that of pure water, both when taking into account  $V_{\text{mix}}^{\text{ex}}$  and not (Figure 2). From Figure 2 it can be assumed that the density of gypsum solution is the same as that of pure water. However, in order to maintain as accurate as possible it is decided to calculate gypsum solution density by taking into account  $V_{\text{mix}}^{\text{ex}}$ .

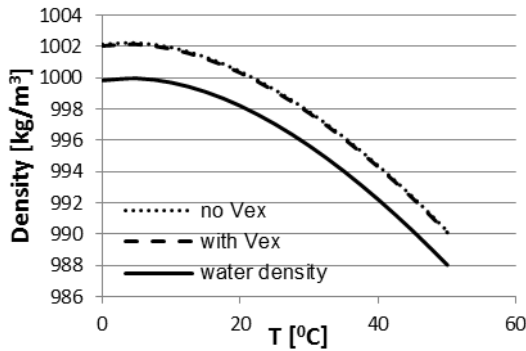
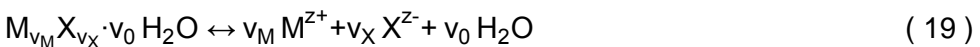


Figure 2: Density of water and saturated gypsum solution

#### 2.2.4 Equilibrium constant

Once the ions and the water activities are calculated it is possible to determine the equilibrium constant for the dissolution and the crystallization reaction for a given salt, equation ( 19 ).



of which the equilibrium constant  $K_{\text{MX}}$  can be determined by the following equation:



$$\ln K_{MX} = v_M \ln a_M + v_X \ln a_X + v_0 \ln a_w \quad (20)$$

where  $v_M$ ,  $v_X$  and  $v_0$  are the stoichiometric numbers of cations, anions and water molecules respectively. The ratio of the equilibrium constant calculated for real activities and molalities, and temperature dependent equilibrium constant  $K_0$  at zero ionic strength, determines the level of saturation  $U$ , and thus crystallization or dissolution [4].

$$U = K_{MX}/K_0 \quad (21)$$

One can assume that for low soluble salts, solubility can be calculated from the solubility product (product of concentrations of ions). However, this cannot be considered very accurate when it comes to 2-2 electrolytes. Due to the ion pairing effects, which has been discussed before, it cannot be safely assumed that concentrations of ions are equal to the solubility of the solid phase, as a significant number of ion pairs can be present. Therefore, very accurate calculations of solubility can be obtained using the ion activities as these are corrected for the effect of ion pairing.

Since the temperature dependence of all ion interaction parameters was described with equation ( 10), it was suggested to use the same equation for the temperature dependence of the equilibrium constant  $\ln K_0$  [8].

For gypsum, the equilibrium constant was determined from solubility data taken from the paper of [11] and Azimi et al. [14], based on equation ( 22) [12]:

$$m_{CaSO_4 \cdot 2H_2O} = \sqrt{K_0}/\gamma a_w \quad (22)$$

Using least square analysis, equation ( 10) was fitted according to obtained data and corresponding parameters, listed in the Table 2.

**Table 2:** Fitting parameters for temperature dependent solubility constant  $\ln K_0$

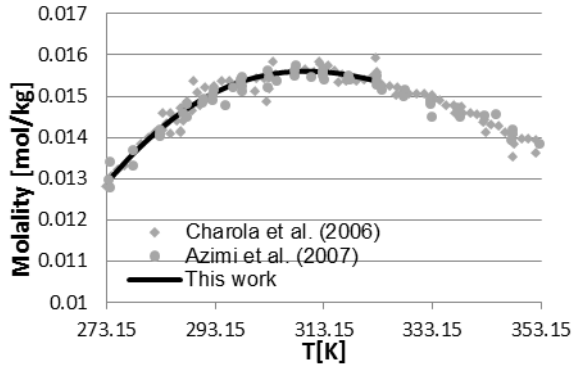
$q_1$	$q_2$	$q_3$	$q_4$	$q_5$	$q_6$
-10.23145825	-25770	-137.6	0.1747	0	0

Figure 3 shows that the calculated gypsum solubility, obtained from the temperature dependent solubility constant  $K_0$ , is in a good agreement with the experimental data, up to a temperature of 50°C.

### 2.2.5 Heat capacity of gypsum and gypsum solution

In the case of the solid phase of calcium sulphate dihydrate and its anhydrite, the heat capacities are 1455 J/kgK and 732 J/kgK respectively. In general, the heat capacity of a salt solution represents the sum of the heat capacities of the solvent, dissolved ions and the capacity which results from the interaction between ions and with the solvent. In case water is the solvent, the heat capacity of a solution can be assumed to be

equal to the heat capacity of pure water, as the presence of ions has an insignificant influence [4]. Since gypsum solution is already characterised by its low concentration, it is feasible to assume that its heat capacity is equal to that of pure water, with a value of 4180 J/kgK.



**Figure 3:** Solubility of gypsum calculated with equation ( 22), taking into account  $K_0$  determined from function (10)

### 2.2.6 Viscosity, surface tension and heat of dissolution

Viscosity and the surface tension are the solution properties that could have an impact on the moisture storage and transport in porous materials. However, in the case of the low soluble gypsum, it is again acceptable to assume that the change in viscosity and surface tension is negligible, and thus that both are the same as for pure water. The same assumption is made regarding the heat of dissolution. Since there is a lack of information about this quantity, it is completely neglected from the model. The justification of this decision is again based on the low solubility of calcium sulphate dihydrate.

## 2.3 Transport parameters

### 2.3.1 Diffusion coefficient

Modelling of salt transport in building materials includes modelling the movement of ions within water, driven by the concentration gradient. This is known as diffusion. In order to describe diffusion of a salt, the diffusion coefficient needs to be determined. As for the other salt properties, the diffusion coefficient can be determined for free salt solutions. It is dependent on the concentration and the temperature, although the last has no significant impact [4]. Taking into account the low solubility of gypsum, a concentration-independent value of the diffusion coefficient can be accepted, assuming that the influence of the concentration is insignificant relative to other effects related to the transport inside a porous media. The value of  $1 \times 10^{-9} \text{ m}^2/\text{s}$  was proposed by Colombani and Bert [15] and accepted in this work.

### 2.3.2 Activation energy

Information for the values of the activation energy is not obtained. Nevertheless, taking into account the low concentration of a saturated gypsum solution, it can be expected that this lack will not affect the results.

## 2.4 Kinetics of dissolution and crystallization

The damages of building materials are quiet often caused by the salts present in the pores of materials. The numerical models of heat, moisture and salt transport in porous materials are developed aiming to study and hence mitigate these damages [16]. In the work of Nicolai [4], and thus in Delphin, salt phase transition rates are based on the model of Espinosa et al. [16] and given by the following equations:

$$\sigma^{m_{p,j}} = -k_{sol}(1-U_j)^{g_{sol}} \qquad \sigma^{m_{p,j}} = k_p(U_j-1)^{g_p} \qquad (23)$$

where  $k_{sol}$ ,  $g_{sol}$ ,  $k_p$ ,  $g_p$  are the kinetic parameters for dissolution and crystallization respectively.  $U_j$  is the saturation ratio, discussed in section 2.2.4. In the case of  $U_j < 1$ , dissolution will take place, while for  $U_j > 1$  crystallization will occur. In order to develop an accurate and reliable numerical model it is necessary to obtain and evaluate the kinetic parameters from the experimental data. As calcium sulphate dihydrate is known for its low solubility, there are limited data regarding the kinetic parameters for dissolution and crystallization in porous materials.

However, Serafeimidis and Anagnostou [17] studied the gypsum precipitation and obtained  $5 \times 10^{-7} \text{ kg/m}^2\text{s}$  and 2 as  $k_p$  and  $g_p$  whereas Jeschke et al.[18] performed rotating disk and batch experiments aiming to determine accurate dissolution kinetic parameters for gypsum. As a result they found almost a linear dissolution rate law, with dissolution constant  $k_{sol} = 1.1 \times 10^{-4} \text{ mmol/cm}^2\text{s}$  and  $g_{sol} = 1.2 \pm 0.2$  from the rotating disc measurement, and  $1.3 \times 10^{-4} \text{ mmol/cm}^2\text{s}$  and  $g_{sol} = 1.2 \pm 0.2$ , from the batch experiments. Nevertheless, they discussed about dissolution kinetic parameters found in the literature, and although they stated that different experimental measurements and set ups can give different results, the order of magnitude for  $k_{sol}$  is  $10^{-4} \text{ mmol/cm}^2\text{s}$ . Since both kinetic parameters are determined without the presence of a porous material, they are expressed per surface area; for precipitation this represents the surface available for crystal growth, while for dissolution it implies the surface area in contact with water and from which dissolution occurs.

However, considering salt phase transitions inside porous materials, the kinetics of dissolution and crystallization are not only dependent on the salt type, but also on the material and its porosity [16]. In order to translate the values of gypsum kinetics to porous materials, some assumptions have to be made. The first one is that the total surface area of pores is available for gypsum dissolution and precipitation. Knowing the pore volume and the pore size, with the assumption of a cylindrical shape of

pores, it is possible to determine the total surface area of pores per cubic meter of material. As an example, the brick type often affected by efflorescence in Belgium has a porosity of 34% and a characteristic pore radius of about  $1\mu\text{m}$  yielding a total pore surface area of  $680000\text{ m}^2/\text{m}^3$ , which lead to material-specific parameters for crystallization and dissolution of  $0.34\text{ kg}/\text{m}^3\text{s}$  and  $140\text{ kg}/\text{m}^3\text{s}$  respectively. The impact of different assumptions regarding the availability of pore surface area is discussed in the next section.

### **3 Application of the model**

Now that all the required parameters are determined, their implementation into the code of Delphin can be made. As the objective is to get an insight into how gypsum is transported and where it crystallizes, a simulation of gypsum wicking experiment is performed. The model is based on the accelerated experiment which is developed at the Department of Geology at KU Leuven [19]. The experiment comprises an initially dry brick sample in contact with a gypsum solution at the bottom face with evaporation allowed only from the top side. The concentration of the gypsum solution is  $0.013\text{ mol}/\text{kg}$ , which is about 80% of a saturated solution. The wicking experiment runs for 5 days at a constant temperature and RH of  $35^\circ\text{C}$  and 20%, respectively. The results reveal that the advective transport of gypsum is very fast; after 4 hours it already reaches the top face (see Figure 4). Since the phase transition is determined by the saturation ratio, the time and the location of gypsum crystallization is determined by when and where the super-saturation of a solution is reached. Knowing that the solubility of gypsum is  $0.015\text{ mol}/\text{kg}$ , saturation of gypsum solution is reached near the surface after 4h. Based on these observations it can be expected that gypsum starts crystallizing near the brick surface, 4 to 5 hours after the start of the experiment, which is confirmed in Figure 5. Additionally, it can be seen that whether 100% or 0.1% of pore surface area is available for crystallization, in both cases crystallization starts after 4h and the location of the precipitation is situated in the top 5mm. However, for the lower versus the higher kinetic constant, the width of crystallized zone is larger while the amount of solid phase is smaller (Figure 5).

Similar observations follow the laboratory study of gypsum transport in porous material reported by Franke and Grabau [20]. Although it was expected that during the laboratory measurements, gypsum would appear at the surface and form efflorescence, the opposite occurred. Contrary to very soluble salts that form efflorescence, gypsum crystallized below the surface in the form of subflorescence, inducing pore clogging and a drop in the drying rate [20]. After analysing the samples they reported that gypsum completely crystallized just below the brick surface at a depth of a few millimetres. The same observations were made from the experiments of Jacek et al.[19].

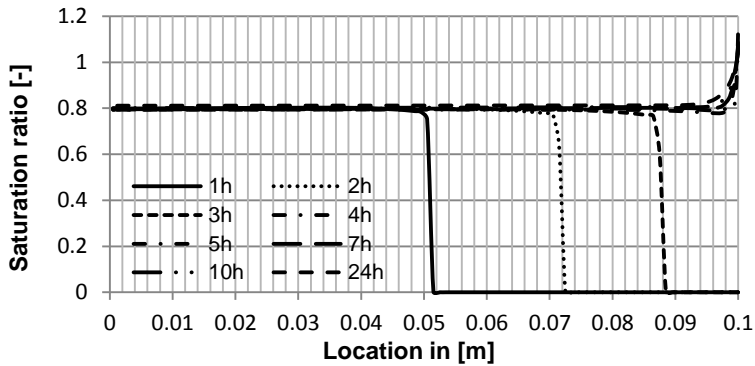


Figure 4: Saturation ratio as a function of time and location

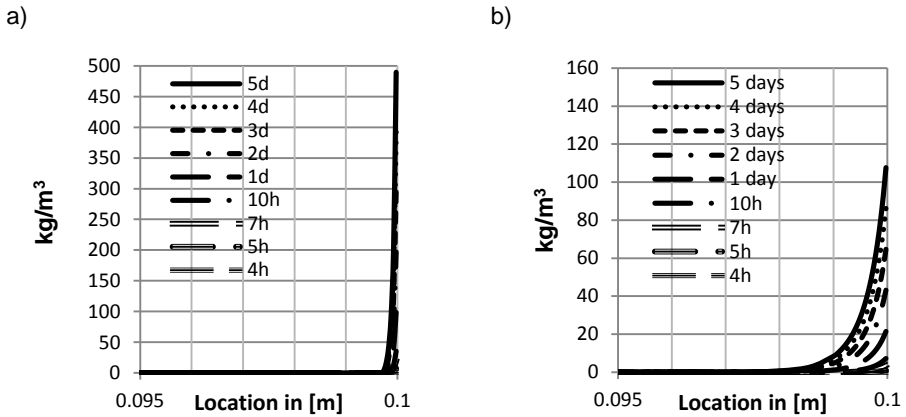


Figure 5: Precipitated gypsum within 5mm below the top surface; a) 100% of pore surface area available for precipitation; b) 0.1% of pore surface area available for precipitation

#### 4 Limitations of the model

While the results from laboratory measurements indicated the drop in the drying rate after 2 to 3 days [19], this observation was not obtained from the simulation. The reason is that the phenomenon of pore clogging is inadequately addressed in the Delphin program

Additionally, even if during the laboratory measurements, gypsum formed efflorescence instead of subflorescence, this would not be the case when it comes to this numerical model. Since the formation of efflorescence is not included in the code of Delphin, regardless of the type of salt that is used in the model, and regardless of the environmental conditions, crystallization will always be located below the surface.

## **5 Conclusions**

The motivation for the numerical implementation and simulation of gypsum transport and crystallization in a porous material is the development of a new type of efflorescence, the so called gypsum efflorescence. Although it has been known for several years already, there are still many uncertainties and questions in relation to the source of gypsum, the recent occurrence and the crystallization behaviour [3]. Therefore, numerical modelling of transport and crystallization of gypsum could provide a better understanding and more insight into the physico-chemical mechanisms behind this phenomenon. Even though Delphin is a software developed for simulation of heat, air, moisture and salt transport and crystallization in porous materials, it does not include gypsum. Mainly due to its low solubility and insensitivity to changes in temperature and relative humidity it is typically not considered as important. On one hand, the low solubility is the limiting factor for the determination of different properties of gypsum solution, but on the other hand many of these properties could be considered as equal to those for pure water. Although these specific characteristics are aggravating factors even for many experimental measurements, it was still possible to accomplish the parameterization of the solid phase as well as of a solution. The Pitzer ion interaction approach was proven to be applicable for the description of the basic physical properties in this case as well as for highly soluble salts.

The initial application of the model is a simulation of a gypsum solution wicking experiment. Based on this simulation, several observations were made. First of all, it was seen that despite the low solubility, gypsum is transported via advection and diffusion, like any other salt. Although transport is also dependent on the material properties, gypsum solution reaches the top surface of a sample after only a few hours, where in the same time frame, it becomes fully saturated. When oversaturation of the solution was obtained near the surface, gypsum started precipitating. Moreover, it was noticed that even after 5 days of the experiment, the total amount of crystallized gypsum was located just below the surface. However, the width of crystallized zone and the amount of precipitated gypsum depend on the magnitude of the kinetic constant. Although similar observations were found from the gypsum solution wicking experiments conducted in the laboratory, this numerical model has several limitations. First of all, pore clogging is not included in the code of Delphin in a sufficient way. While under the laboratory conditions, a drop in the drying rate was noticed after several days, this cannot be achieved with the present model. Secondly, the motivation for this work was the development of gypsum efflorescence. However, the impossibility of the simulation of efflorescence in general is another limitation of the model.

Despite of these limitations and deficiencies, this model is still a great starting point for further research and additional improvements. Since the validation of the numerical model of gypsum transport and crystallization is the subject of ongoing research, first the present limitations will have to be

addressed. Additionally, the interaction with other ions and salts will be studied and included in the model, in order to analyse whether there is a significant change in the gypsum solution characteristics which could be the reason for the development of the new efflorescence type.

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