The influence of sorption hysteresis on diffusion coefficients represented with different moisture potentials

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ABSTRACT

This paper continues the discussion in a previous paper [Saeidpour and Wadsö doi:10.1016/j.cemconres.2016.02.003] where a clear effect of sorption hysteresis was seen in moisture diffusion coefficients for cement-based materials. Coefficients with vapor content as potential (D_v) had different values depending on whether the sample was in absorption or in desorption. In this paper we recalculate these D_v coefficients into coefficients with other potentials and draw them as a function of different potentials. The aim is to see if the effect of hysteresis disappears with an optimal choice of representation. The best choice was to draw D_v is as a function of the degree of saturation (concentration, moisture content).

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1. Introduction

A common approach in the study of transport of water vapor in cement-based materials is to combine a sorption isotherm with a transport coefficient. This is not trivial as cement-based materials are known to show sorption hysteresis and scanning behavior and a significant effort has been put into describing this complex path (history) dependent property [1–5]. In addition, transport coefficients (diffusion coefficient and permeability) are functions of the moisture state, for example of relative humidity (RH) or moisture content (MC) [6–9] rather than constant values. In a recent paper [10] we also showed that at least for cement mortars made with ordinary Portland cement (OPC) there is a significant difference between the moisture diffusion coefficients when a mortar is on the absorption or on the desorption limbs of the sorption isotherm, even if the two values are determined in the same RH interval. We then expressed the diffusion coefficient with vapor content as potential as this is the most natural choice for the steady-state cup measurements that we did.

A problem with moisture transport coefficients is that they can be expressed using many different potentials. This is in contrast with for example heat transport which is always treated using temperature as potential; or diffusion of chloride ions in concrete where concentration (mass of ions per volume material) is the preferred potential. For moisture transport we can use vapor content (v, mass vapor per volume air), volumetric moisture content (c, mass of moisture per volume material) or a dozen other potentials. This opens for the question of which of these possibilities that is best in the sense that it gives the smallest dependence of the transport coefficient on the potential or whether the

system is in absorption or desorption. Our previous results [10] gave 3–4 times higher diffusion coefficients in desorption than in absorption in the RH-range 75–95%; in a similar study on self-levelling flooring compounds Anderberg and Wadsö [11] found a 30% higher transport in desorption than in absorption in a similar RH-interval. We know of no other studies of this subject.

It is well known that sorption hysteresis above 50% RH is caused by that the filling (absorption) and emptying (desorption) of a pore does not take place at the same RH [1,5,12]; the RH for emptying of a pore is lower than the RH at which the same pore is filled. This could also affect the transport, as the rate of transport is significantly higher in a water filled pore than in a pore in which vapor diffuses [10]. As there are many different pore sizes, pore shapes, pore connections etc. in cement based materials, the sorption situation is complex, and it is not possible to theoretically determine the values of transport coefficients with different potentials and on different limbs of the sorption isotherm.

It is the aim of this work to determine how the transport coefficients should be represented to introduce a minimum of sorption hysteresis in the transport coefficient. This includes both the potential used for the coefficient and what potential it should be a function of. Originally we evaluated $D_v(\varphi)$, where φ is the relative humidity, i.e., v/v_{sat}, which at isothermal conditions essentially equals $D_v(v)$ (we here assume that the ideal gas law holds). Some examples of other alternatives are $D_v(c)$, $D_c(v)$ and $D_c(c)$. In this study we recalculate D_v to other potentials and present these transport coefficients as functions of different potentials.

2. Experimental

The experimental results that we use in the present paper are from two standard mortars of ordinary Portland cement (OPC) with water/

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cement-ratios (w/c) of 0.5 and 0.4. The sample preparation is described in reference [3] and the transport measurements with the cup method and the evaluation of D_v as a function of RH are discussed in detail in reference [10]. The measurement was done in two steps. First water saturated disk-shaped samples were placed as lids on cups with internal salt solutions with 33.1, 57.6, 85.1, 94.6 and 97.6% RH. The RH outside the cups was 75.5%, so this part of the measurement gave values measured in desorption. The samples were weighed regularly until constant mass change rates (flow) were reached, from which $D_v(\varphi)$ was calculated. In a second step the cups were opened and the salt solutions were removed. The samples were then dried in 33.1% RH, after which the cups were closed again (with the same salt solutions as mentioned above) and the measurement continued. From this step of the measurement $D_v(\varphi)$ in absorption was calculated when the flow reached steady-state. The sorption isotherms needed for the recalculations between different potentials were determined using a sorption balance and taken from reference [3].

3. Evaluation

In the cup method the vapor content is the natural potential (driving force) to calculate diffusion coefficients with [10], but it is also possible to use other potentials to calculate diffusion coefficients. One example is using volumetric moisture content (concentration) as this is the natural potential in the dynamic sorption method to measure transport coefficients [2,13]. It is possible to recalculate from coefficients based on one potential to coefficients based on another potential if the relationship between the potentials is known. Changing the potential gives other numerical values, (often) other dependences on the moisture state, and (in most cases) other units of the transport coefficient.

These recalculations are based on viewing a steady-state transport case from the viewpoint of the two potentials of interest. If we have the transport coefficient for potential a and wants to have the transport coefficient for potential b, we begin by stating Fick's law with these two potentials (the recalculations could also have been made using Δ instead of differential d:s):

$$q_m = -D_a \frac{da}{dx} \tag{1}$$

$$q_m = -D_b \frac{db}{dx} \tag{2}$$

Here, q_m (g s^{-1} m^{-2}) is the mass flux, which must be equal in the two equations as the above two equations are for the same transport case. We can this equate the right sides of the two equations and rewrite to

$$D_b = D_a \frac{da}{db} \tag{3}$$

We can thus recalculate transport coefficients from one potential to another if we know how one of the potentials changes when the other changes. For the trivial case of vapor content v and relative humidity φ, we get.

$$D_\phi = D_v \frac{dv}{d\phi}, \tag{4}$$

where

$$\frac{dv}{d\phi} = v_{sat}, \tag{5}$$

as the relative humidity is the vapor content divided by the saturation vapor content v_{sat}.

For the more complex case of vapor content v (g m^{-3}) and volumetric moisture content (concentration) c (g m^{-3}) we get the following relation:

$$D_c = D_v \frac{dv}{dc}, \tag{6}$$

where

$$\frac{dv}{dc} = \frac{v_{sat}}{\rho \frac{du}{d\phi}} \tag{7}$$

Here, D_v (m^2 s^{-1}) and D_c (m^2 s^{-1}) are transport coefficients with vapor content and concentration as potentials, respectively, ρ is density of the material (g m^{-3}) and $du/d\varphi$ is the slope of sorption isotherm, where u (g g^{-1}) is the specific moisture content (gram water per gram dry material) and φ (Pa Pa^{-1}) is the relative humidity.

In this paper we have also used the degree of saturation S (m^3 m^{-3}) as potential. This is the fraction of the pore volume that is filled with moisture. The degree of saturation is related to the concentration as follows:

$$S = \frac{c}{p \cdot \rho_w}, \tag{8}$$

where p (m^3 m^{-3}) is the porosity and ρ_w (g m^{-3}) is the density of liquid water. It can also be calculated from the volumetric moisture content and the maximal volumetric moisture content (when the pore system is assumed to be completely filled):

$$S = \frac{c}{c_{\max}}, \tag{9}$$

As both porosity and water density are constants (for one material), the degree of saturation is proportional to concentration for a certain material and at a certain temperature.

Finally, we have used the fundamental potential Ψ (g s^{-1} m^{-1}), which can be seen as the potential defined in such a way that the transport coefficient always is unity:

$$q_m = \frac{d\Psi}{dx} \tag{10}$$

This potential has found use in building physics calculations (see for example reference [8]) and has an advantage when calculations are based on transport data from cup measurements, as these measured data can be used directly in the calculations without the calculation of transport coefficients. It may seem odd to include this potential with a constant diffusion coefficient in a paper on diffusion coefficients, but the moisture dependence is here built into the potential and not the coefficient. Therefore, to see if the fundamental potential will reduce the influence of hysteresis we have to look at the fundamental potential itself as a function of different other potentials.

The fundamental potential can be evaluated directly from our cup results (reference [8], p. 525). For each internal RH (φ) in the cups the fundamental potential is

$$\Psi(\phi) = q_m \cdot L \tag{11}$$

where L (m) is the thickness of the cup sample. Note that from this definition we find that the fundamental potential for the common RH outside the cups is by definition zero as we have zero flux when the internal and external RHs are the same. The reference point of the fundamental is thus dependent on how the experiment is conducted, but this is of no importance as only differences between different Ψ-values are used (cf. enthalpy where the value at 25 °C and 1 atm is the most common reference value). In the present measurements the reference (zero) point for the fundamental potential is at 75.5% RH.

4. Results and discussions

4.1. D_v and Ψ as a function of RH

The D_v and Ψ as a function of RH for OPC samples are shown in Fig. 1. The black lines are for samples on the desorption curve and the red lines are for samples on the absorption curve. Note that D_v is evaluated as mean values in different RH intervals, while each cup measurement interval gives one Ψ-value at the end of the interval.

4.2. D_v and Ψ as a function of S

The diffusion coefficient D_v of OPC samples as a function of S is shown in Fig. 2. Sorption isotherms for same materials were taken from reference [3] and used to calculate moisture content. The degree of saturation was not measured, but is calculated as moisture content divided by the moisture content at 97.6% RH (the degree of saturation at 97.6% RH is assumed as 1.0) as 97.6% is the highest value in our transport measurements and close to the critical RH where all pores are filled by pore solution except large capillary pores [3,14]. As the sorption isotherms were not measured over RH = 95%, the moisture content at RH = 97.6%, was assessed by assuming that the slope of each sorption isotherm is constant from 85% RH to 97.6% RH. The values of the moisture content at saturation were 0.075 and 0.052 $g_{water}\ g_{mortar}^{-1}$ for w/c 0.5 and 0.4, respectively. This compares reasonably well with values 0.067 and 0.055 $g_{water}\ g_{mortar}^{-1}$ calculated using Powers' model of cement paste porosity given in Eqs. 21–22 in reference [15]. The cement composition was (fractional mass) 0.527, 0.193, 0.106, and 0.074 for C_3S, C_2S, C_3A and C_4AF, and we used a specific volume of non-evaporable water of 0.72 [16]. However, note that the results are not critically dependent on the value of the maximal moisture content as both absorption and desorption are scaled with the same factor. In Figs. 2a and b the difference between the results in absorption and desorption is smaller than in other representations tested.
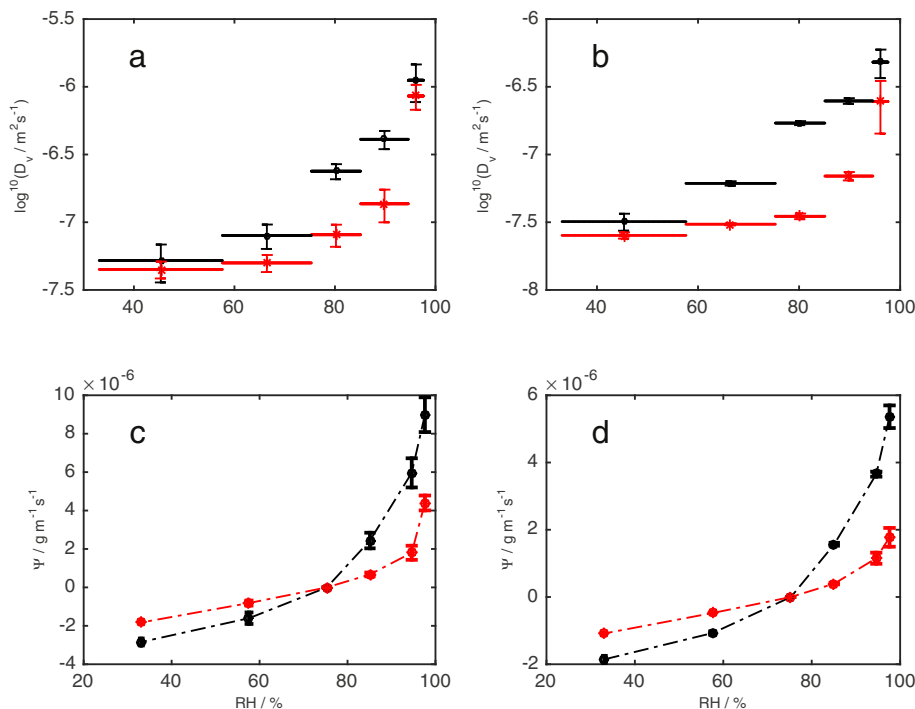
Place Fig. 2 here.

4.3. D_c as a function of RH and S

Fig. 3 shows D_c (calculated from D_v by Eqs. 6–7) for samples in absorption and desorption as a function of RH and S. The results show similar influence of hysteresis as D_v as a function of RH. Note that the calculations with Eqs. 6–7 brings an added uncertainty into these coefficients; especially from the slope of the sorption isotherm (no error bars could be calculated).

4.4. General discussion

Looking at the results in Figs. 1-3, it is seen that Fig. 2b shows the smallest difference between absorption and desorption, closely followed by 2a. This indicates that when the diffusion coefficient with vapor content as potential (D_v) is used as a function of the degree of saturation (or moisture content or concentration) the effect of absorption/desorption does not need to be taken in to account. However, this study was rather limited and this tentative conclusion should be further tested.

It may seem odd that a transport coefficient using one potential (vapor content) should be used together with another potential (degree of saturation, concentration) describing the state of the water. However, it may be natural that two potentials are used together to reduce the effect of hysteresis, one to describe the conductivity and one to describe how the conductivity changes with a change in moisture content/state. Below we give some arguments for that the best choice of potentials that we have indicated above is the best representation also in terms of the physics of the processes. However, these arguments are rather weak and should only be seen as the start of a discussion about this.

Moisture transport in porous materials is a combination of vapor and liquids flow. The most physical way of representing the vapor transport part (Fick's law) is probably by using vapor pressure, which is equivalent to using vapor content. When it comes to liquid flow (Hagen-Poisseuilles and Darcy's laws), this is treated in terms of pressure of
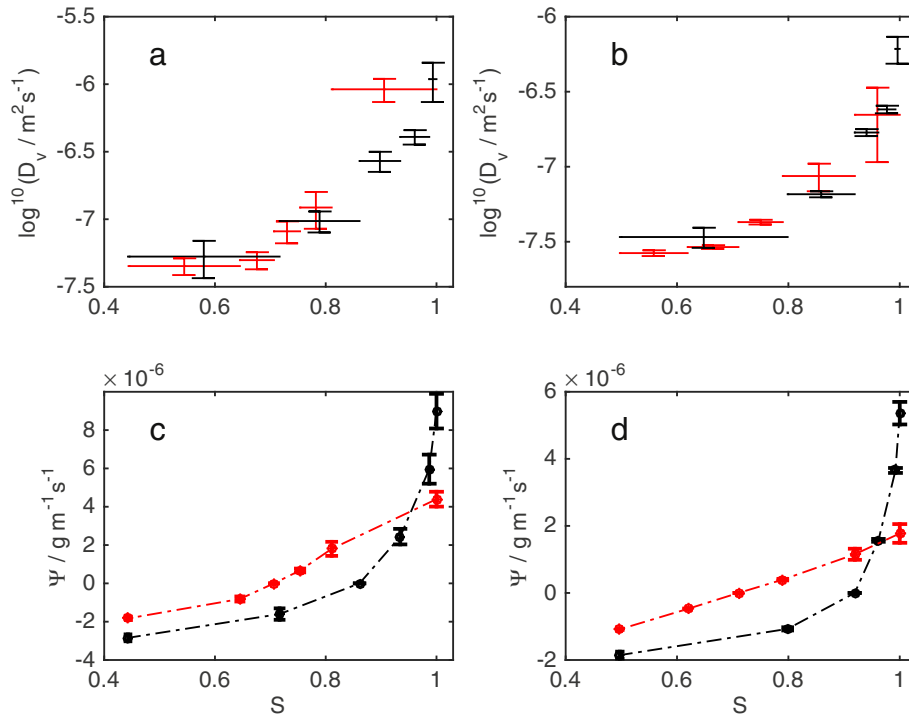

Fig. 1. Diffusion coefficients (D_v) as a function of RH (a): OPC mortar w/b = 0.5, (b): OPC mortar w/b = 0.4, Ψ as a function of RH (c): OPC mortar w/b = 0.5, (d): OPC mortar w/b = 0.4. The black lines are on the desorption curve and the red lines are on the absorption curve. The error bars are the standard deviations calculated from three replicates.

Fig. 2. D_v as a function of degree of saturation (S) (a): OPC mortar w/b = 0.5, (b): OPC mortar w/b = 0.4. Ψ as a function of S (c): OPC mortar w/b = 0.5, (d): OPC mortar w/b = 0.4 The black lines are on the desorption curve and the red lines are on the absorption curve. The error bars are the standard deviations calculated from three replicates.

the liquid. In porous systems where the pressures originate from the capillary action (not from external pressure), the pressure can be written in terms of relative humidity by the Kelvin equation. As vapor content and relative humidity only differ by a constant factor under isothermal conditions, we can conclude that both the vapor and the liquid flow components naturally can be written in terms of vapor content

in our case. Although one can use concentration based moisture potentials, these will not have the same strong connection to the physics of the transport processes.

The situation is possibly different when it comes to how the moisture state influences the value of a transport coefficient. It is generally believed [17] that at low moisture levels there is mainly vapor flow
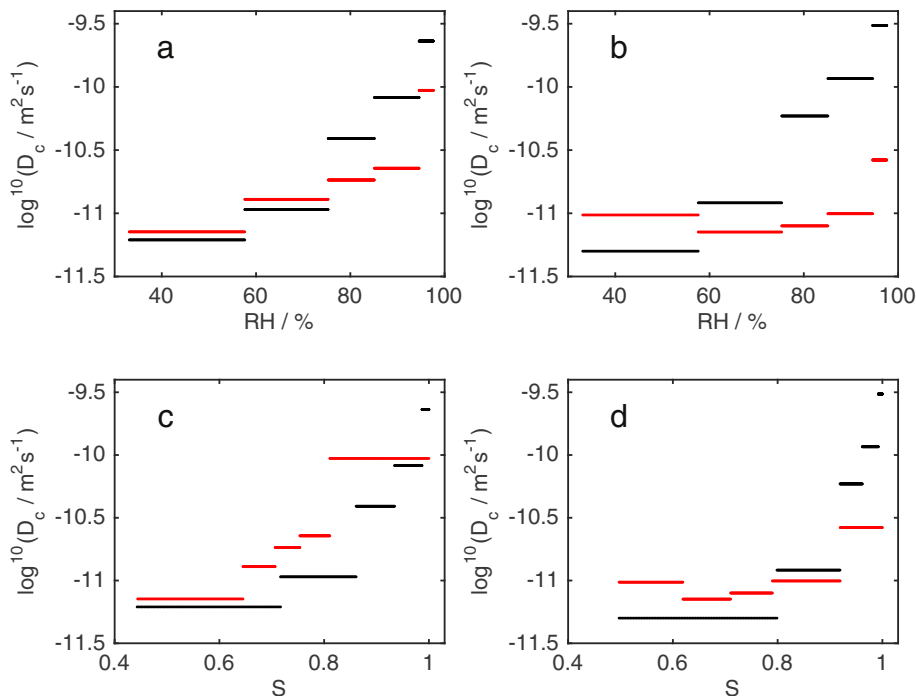

Fig. 3. Moisture diffusivity D_c as a function of RH (a): OPC mortar w/b = 0.5, (b): OPC mortar w/b = 0.4. D_c as a function of S (c): OPC w/b = 0.5, (d): OPC mortar w/b = 0.4. The black lines are on the desorption curve and the red lines are on the absorption curve. Note the logarithmic y-axes.

and at higher moisture levels there is a combination of vapor and liquid flow. At least above 50% RH the liquid part is the most important as liquid flow is so much higher than vapor flow, all other parameters kept equal. If we look at a porous material at two moisture states with different amounts of liquid water, it does seem natural that the state with a higher moisture level (higher moisture concentration) will correspond to a higher flow rate; so that concentration should be a more proper potential to judge the variations in transport coefficients than, e.g., RH. We can envisage a porous material with no pores in a certain pore radii range. If the moisture state is increased through this area where there are no pores, the RH will increase, but very little moisture will be taken up and the transport coefficient will not change. It may thus be natural that transport coefficients are represented as a function of concentration based potentials, like the degree of saturation.

The above reasoning is not a rigorous argumentation and it is probable that it is a too limited approach to look at the potential of the coefficient and the potential it is a function of as two separate problems as we did above.

5. Conclusions

Expressing the transport coefficients using vapor content as a function of degree of saturation (essentially moisture content or concentration) gave the lowest difference between data in absorption and desorption in our study.

Acknowledgment

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