

# Diffusion of water vapour in cement-based materials: is Fick's law valid?

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## ABSTRACT

It is necessary to understand moisture transport in cement based materials to understand processes such as chloride ingress and frost damage that influence the service life of structures. However, moisture transport is a complex phenomenon as both sorption and transport are nonlinear functions of the moisture state and also depend on the moisture history (wetting/drying). There are different methods to measure transport coefficients in cement-based materials. Steady-state methods (for example the cup method) give diffusion coefficients with vapour content as potential (driving force), while non-steady state methods (sorption methods) give diffusivities (with moisture content as potential). We have used a method to simultaneously measure the diffusivity and the sorption isotherm, which also makes it possible to calculate the diffusion coefficient with different potentials. In this method a small sample is exposed to step-wise changes of relative humidity while its mass is continuously measured in sorption balance. The mass change after each relative humidity step is normally used to calculate the diffusivity as a function of moisture state using Fick's law of diffusion. However, it has long been known that polymeric materials – both natural and synthetic – sometimes do not give results from sorption measurements that can be interpreted by Fick's law only, and we have now assessed whether our results for cement based materials are "Fickian". The results clearly show that Fick's law of diffusion cannot completely describe the vapour transport in cement-based materials as different deviations from Fick's law are seen in different relative humidity intervals, depending on whether measurements are made in absorption or desorption, or when a transition is made from one of these modes to the other (scanning).

## 1. INTRODUCTION

The sorption method is a method to evaluate the diffusivity from measurement of the rate of vapour uptake or vapour loss by sample. This method is used extensively for many materials for example polymers, both synthetic (Petropoulos, Sanopoulou et al. 2011), and natural, such as wood (Wadsö 1994). The experimental process is to expose a sample with the thickness  $l$  in equilibrium with a certain vapour atmosphere at constant temperature and measure the mass increase/decrease, i.e. and the rate of uptake/loss of vapour to calculate the diffusivity. One version of this method is used to evaluate both the diffusivity and the sorption isotherm from the same measurement; this has for example been done for self-leveling flooring compounds, based on calcium aluminate cement, calcium sulphate and Portland cement (Anderberg and Wadsö 2008).

Mass diffusion process is described with Fick's first (Eq.1) and second laws (Eq.2).

$$F = -D_c \frac{\partial c}{\partial x} \quad (1)$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_c \frac{\partial c}{\partial x} \right) \quad (2)$$

Here  $F$  (kg/m<sup>2</sup>s) is the flux,  $D_c$  (m<sup>2</sup>/s) is the diffusivity,  $c$  (kg/m<sup>3</sup>) is concentration and  $x$  (m) is distance.

The solution to Fick's second law when a step change of the potential is made on the boundary of a sample with one-dimensional transport (a "slab") is an infinite series, but simplified solutions can be used to calculate the mean diffusivity in the measurement interval. The most common of these is to use the initial slope of the mass change plotted as a function of the square root of time, or to calculate  $D_c$  from the time to half sorption (Crank 1979). A common complication with Fick's law is that the diffusivity is not constant as it is a function of the moisture content (gradient). In the this case of the sorption method, the initial slope of the mass change as a function of the square root of time is still linear, and the evaluated diffusivity will be a weighted average of the diffusivity in the measurement interval.

It has been found that some sorption measurements do not give results that can be reconciled with Fick's law. Most commonly such so called non-Fickian behavior has been found for synthetic and natural polymers (Petropoulos, Sanopoulou et al. 2011). In extreme cases the initial mass change is not linear with respect to the square root of time, but to time; this is called case II (Hansen 1980; Petropoulos, Sanopoulou et al. 2011).

One important experimental factor that can give non-Fickian behavior is a limited mass transfer on the surface of a sample (Hansen 1980). Such results show diffusion with a slight delay and an S-shaped curve of mass change as a function of the square root of time (Hansen 2010). However, a limited mass transfer at the surface is actually a Fickian phenomenon, and should possibly not be termed “non-Fickian”.

This study is part of the Marie Curie initial training network TRANSCEND program funded by the European community with the aim of understanding water transport in concrete and cement-based structures in the presence of supplementary cementitious materials (SCMs). We use the sorption method to measure the diffusivity of these materials. The present paper is limited to the question of whether the measured curves are Fickian or non-Fickian, and it is clear that the majority of our results do not show a completely Fickian behavior and it is thus not possible to evaluate with the solution of Fick’s second law using the methods outlined above. The authors of this paper believe that although the boundary layer resistance is an important factor for non-Fickian behavior in polymer samples, this is not the explanation to why we see non-Fickian behavior in cement based materials.

## 1. Materials and methods

### 1.1. Materials

The samples tested were cement pastes with three different binders: OPC (CEMI), OPC with 10% silica fume and OPC with 70% slag (CEMIII) with a water to cement ratio of 0.5. The samples were cast in stainless steel tubes (length 2 or 1 mm, inner diameter 5.5 mm). The samples were thus disks with 5.5 mm diameter and thickness of 1 or 2 mm. The aim was to have well-defined sample geometry with one-dimensional moisture flow. The samples were hydrated in sealed containers at 20°C for 90 days and then partially saturated by absorbing water from wet clothes for two weeks.

### 1.2. Methods

The samples were placed in a sorption balance (DVS-1000, Surface Measurement Systems Ltd, UK). The sorption balance can generate different relative humidities by mixing different proportions of dry and saturated with water nitrogen gas streams. The mass of the samples is continuously measured with an analytical balance in the sorption balance while it is exposed to an RH program. A measurement can be done in both absorption and desorption steps.

The measurements reported here were made in initially partially water saturated samples. The RH program was composed of an initial series of

desorption steps, followed by absorption steps, and ended with a series of desorption steps down to 0% RH. The complete program was desorption 95-90-80-70-60-50-40-30%, followed by absorption 30-40-50-60-70-80-90-95%, and ended by a second desorption 95-90-80-70-60-50-30-25-20-15-10-0% RH. The measurements were thus done in many small RH-ranges. Figure 1 shows an example of one complete RH step program that was used in this study. The time at each RH level depends on how quickly equilibrium is attained as the program continues to the next RH level when the absolute mass change rate is less than 0.0001 per cent of the sample mass per minute. However, there is also a maximal duration of each RH-level of 2000 min. A full measurement took approx. 20 days.

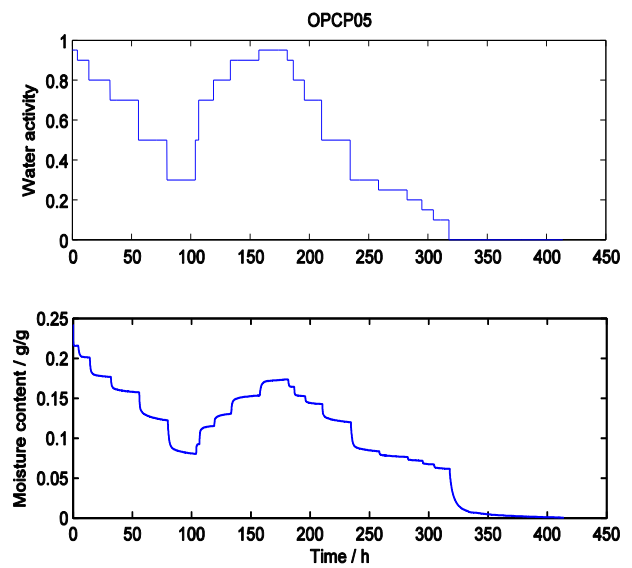


Figure 1. Typical relative humidity stepwise changes and the sample response

### 1.3. Evaluation method

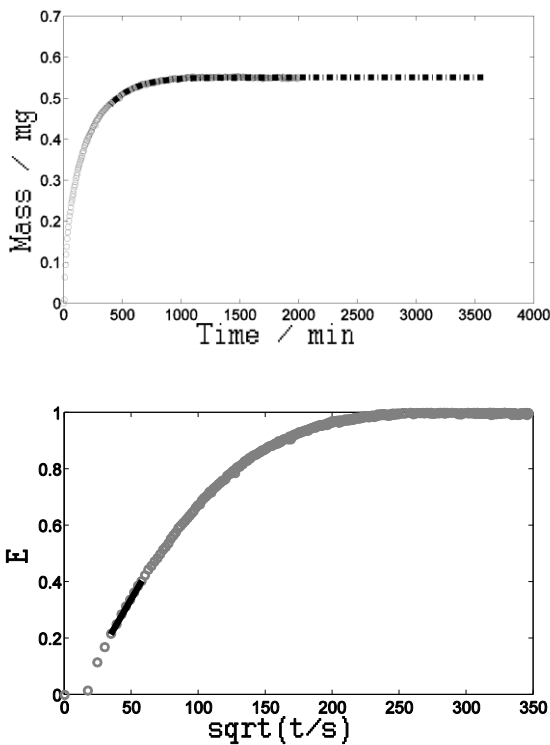
To calculate the diffusivity, the mass response to each RH step change is evaluated separately. First the final part of mass change as a function of time was curve fitted and extrapolated using an exponential function to find the equilibrium mass (at infinite time). A parameter  $E$  is defined as  $E = \Delta Mt / \Delta M \infty$ , where  $\Delta Mt$  and  $\Delta M \infty$  are the mass changes at time  $t$  and after infinite time. Then the corresponding  $E$  vs. square root of time ( $\sqrt{t}$ ) curve (sorption curve) is plotted ( an example is seen in Figure 2).

For each step change in RH an equation based on Fick’s law was used to calculate diffusivity (Eq.3).

$$D_c = \frac{\pi x l^2}{4} \left( \frac{dE}{d\sqrt{t}} \right)^2 \quad (3)$$

Here  $l$  (m) is the half of the thickness of sample and  $D_c$  ( $m^2/s$ ) is the diffusivity with moisture content

as potential. The first linear part of the sorption curve is used to calculate diffusivity.



**Figure 2.** An example of (a): mass response and final mass extrapolation (---) (b): corresponding sorption curve for an OPC paste sample in absorption from RH=50 to 60%

The first linear part of the sorption curve is used to calculate  $dE/d\sqrt{t}$ . As is seen in Figure 2b, there is a significant linear part of the curve that can be used to calculate this derivative. Note that the slight initial delay of the mass response in the present case are caused by a combination of the inability of the sorption balance to make a perfect step change of the RH and the limited mass transfer at the surface. The latter effect is, however, small as the sorption balance has a continuous gas flow over the surfaces of the sample. It has been shown that even when there is a slight initial non-linear part on the curve, the linear part can in practice be used to calculate the diffusivity (Wadsö 1994).

## 2. Results

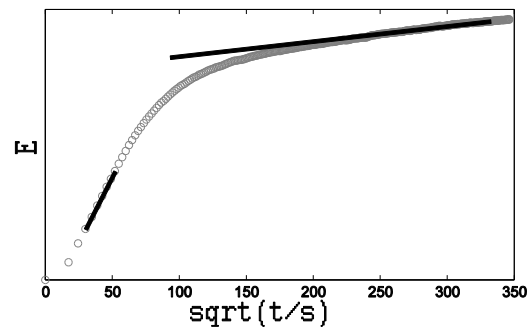
As will be shown below, most of our curves are not easy to evaluate using the above standard method. We show this by plotting our mass change results as a function of the square root of time. If Fick's law governs the mass change process, this should result in curves with a shape as in Figure 2b.

### 2.1. Desorption for higher RH steps (90-70%)

In this range there is an initial fast sorption regime followed by slower sorption regime. These can be

seen as two almost linear parts in the sorption curve. These kinds of curves were seen in both the first and second desorption in this range.

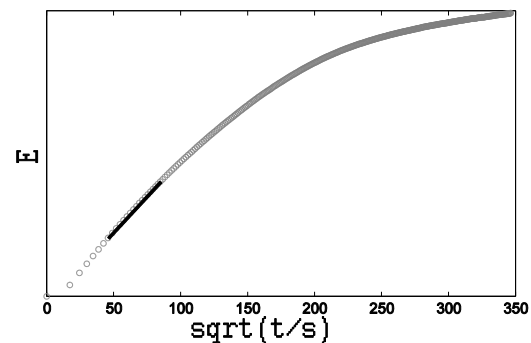
These results can be viewed in terms of the general non-Fickian model by Berens and Hopfenberg (Berens and Hopfenberg 1978). In this model the sorption curve is a sum of Fickian sorption and one or more non-Fickian parts with other time scales. In this example the Fickian and the non-Fickian processes have different and separated time scales and we can possibly still use the initial part of the curve to evaluate the Fickian macro diffusivity. Studies on wood showed that the initial parts of curves such as those shown in Figure 3 were not influenced by the non-Fickian behaviour. However, the diffusivity calculation should only use that part of the mass increase that is related to the Fickian process. Otherwise the calculated diffusivity will be lower than diffusion coefficient measured with steady-state method (cup method) (Wadsö 1993).



**Figure 3.** An example of non-Fickian behaviour at high RH and desorption (OPC paste in second desorption RH: 90 to 80%). Two different close to linear parts can be seen.

### 2.2. Desorption for lower RH steps (70-30% and 70-0%)

Here the sorption curves show close to linear (Fickian) behaviour until more than half of sorption has taken place, but the curves do not level off as would be expected for completely Fickian behaviour (Figure 4). In contrast to the result shown in Figure 3, the non-Fickian parts do not show a linear behaviour as a function of the square root of time.



**Figure 4.** An example of behaviour for desorption at low RH (OPC paste in second desorption, RH: 40 to 20%).

### 2.3. Absorption for all RH steps (30-95%)

In this study the samples were in absorption mode from RH=30% to RH=95% after first desorption. In some RH intervals the curves are clearly Fickian (Figure 5) but in other intervals the final part is not quite Fickian, and it is difficult to assess whether they are Fickian or non-Fickian. Longer measurements are necessary in these steps to be able to correctly evaluate the results.

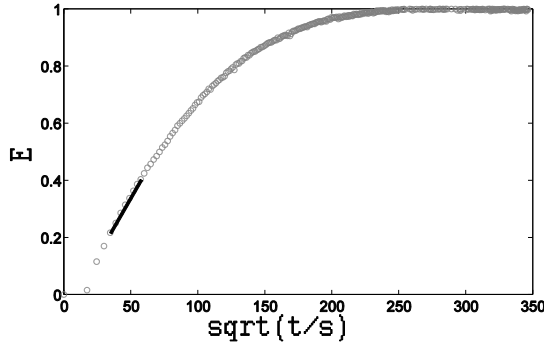


Figure 5. An example of Fickian behaviour in absorption for OPC paste, RH=50 to 60%

### 2.4. Changing from desorption to absorption curves

In the first step after changing from desorption to absorption mode a complex behaviour was seen in all samples. The mass of the samples increased at the beginning as expected, but then started to decrease at the end of the step (Figure 6). This behaviour was observed in the first two steps of absorption for all samples (RH=30 to 40% and RH=40 to 50%) and is possibly related to the scanning behaviour.

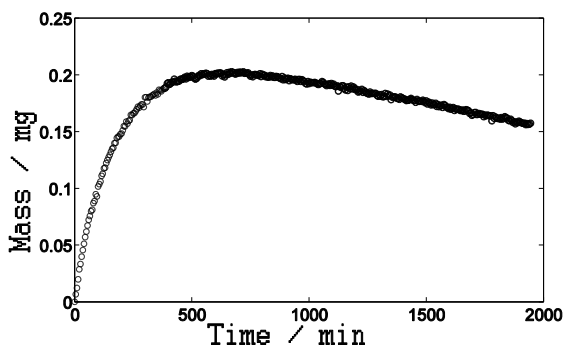


Figure 6. An example of mass decrease in changing from desorption to absorption, OPC paste RH=30-40%

### 3. Discussion

From the results given above, it is clear that sorption of water vapour in cement paste cannot generally be completely described by Fick's law. Although the aim of the present paper is not to explain the origin of the non-Fickian behaviour, we believe that some of the following mechanisms may be responsible:

- Slow diffusion of water in the finest porosity.
- Slow diffusion through the liquid phase of air trapped in inner parts of pores.

It is questionable whether mechanical relaxation models, as are used in used in polymer science to explain non-Fickian behavior, are relevant for cement based materials.

The non-Fickian behaviours seen in the curves above are not caused by experimental limitations, such as external mass transfer resistances, continued cement hydration, or drift in the balance. They are signs of internal sorption processes.

### 4. Conclusion

Fick's law of diffusion is not able to completely describe the water vapour transport in cement-based materials. Internal processes cause the non-Fickian behaviour, but it is at present unknown which these processes are for cement-based materials.

### Acknowledgement

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under grant agreement 264448.

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