EVIDENCE FOR NON-FICKIAN SORPTION IN CEMENT BASED MATERIALS

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Introduction

The diffusion of gases and vapors in solids – for example water vapour diffusion in a construction material – is normally assumed to follow Fick's law of diffusion. However, there are numerous examples in the polymers literature of that the uptake of vapours in – both natural and synthetic – show deviations from Fick's law, i.e., is non-Fickian. There has also been speculations in for example the cement literature that the diffusion cannot be fully explained using only Fick's law.

Whether a system is Fickian or non-Fickian is most commonly judged from the mass change rate after a step change in external vapour concentration. If Fick's law is valid, the mass change is proportional to the square root of time until more than half the sorption has taken place and is practically at equilibrium after about 3.0 square root of the time to half sorption. This is shown in the theoretical solid line in Fig. 1. We call such a result a "sorption curve".
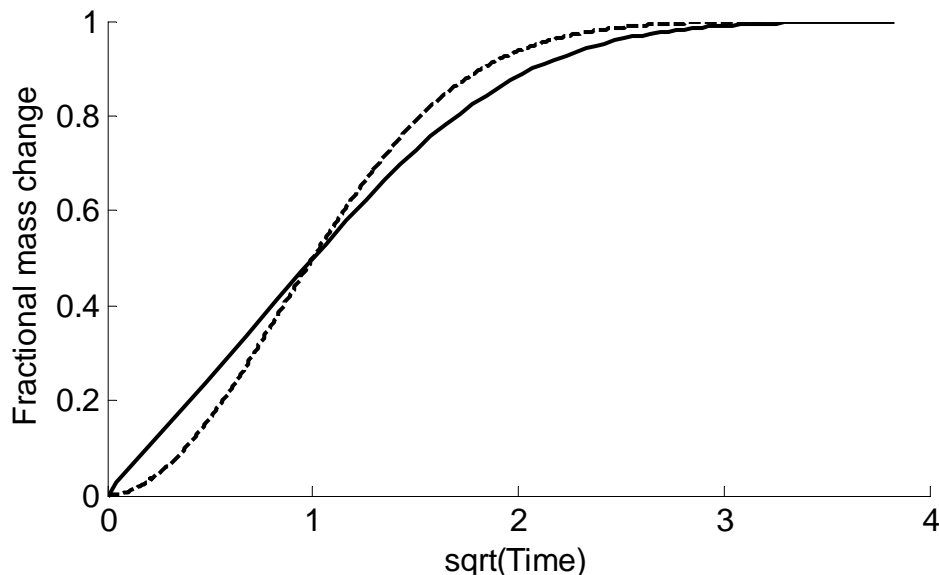

Fig. 1: The calculated fractional mass change as a function of square root of time for two Fickian sorption cases (equations are given by Crank [1]). The solid line is for a case with no (or negligible) external mass transfer resistance and the dashed line is an example of a Fickian sorption curve with a relatively high external resistance. Both curves have been scaled so that the time to half sorption is at time equals 1.0.

Sorption curves commonly have a more or less sigmoid shape as it is difficult to experimentally realize the ideal step-change of conditions of the surface of the sample. The dashed line in Fig. 1 shows this for a calculated case with a substantial external mass transfer coefficient. Another factor that causes sigmoid shapes is a non-ideal RH step; it will in many experimental techniques take some time for the RH to change from one level to another. As both external mass transfer coefficients and non-ideal steps are factors outside the material to be investigated, we do not define the sigmoid curves resulting from these effects as non-Fickian.

Non-Fickian effects are mainly of two types. Either the mass uptake is not a linear function of the square root of time, or there is a much slower attainment of equilibrium than would be expected if the process was governed by Fick's law. Much research in the polymer field has focused around the first of these effects and much has been published on so-called case II diffusion in which the mass uptake is proportional to time as the process is governed by relaxation processes at the front between swollen and un-swollen polymer. The

second – long term sorption – is also seen for polymers and can be modelled, e.g., with a series of exponential function with different time constants.

In cement based materials, it is less likely that sorption is influenced by relaxation, but we and others have observed slow attainment of equilibrium in many experiments, which could indicate that we have non-Fickian processes also in such materials. We here give an example of such a measurement and discuss this result.

Experimental

Sorption measurements were made with a DVS 1000 (Surface Measurement Systems Ltd, London, UK). The samples were disks of different cement pastes with thicknesses of 1 or 2 mm that were cast in stainless steel rings to make the transport one-dimensional. Measurements were made by exposing the samples to the following RH-program: 95-90-80-70-60-50-40-30-40-50-60-70-80-90-95-90-80-70-60-40-20-10-0% RH. Each RH level was kept constant for 2200 min and the mass change was determined. The main aim of the measurements was to calculate the diffusion coefficient [2], but we have also used the results to assess possible non-Fickian behaviour. We here show a one results from our studies; the bulk of our measurements will be reported elsewhere.

Results

When we have made sorption studies on cement pastes and cement mortars we have found that many of the resulting curves cannot be fitted to the Fickian diffusion model, i.e., they are non-Fickian. Figure 2 shows one example. Unfortunately – because of time constraints – we cannot run each step in our measurements for more than about 33 h (2200 min), but the result is distinctly non-Fickian as there is still a substantial mass uptake after 3.0 times to half sorption (cf. Fig. 1).
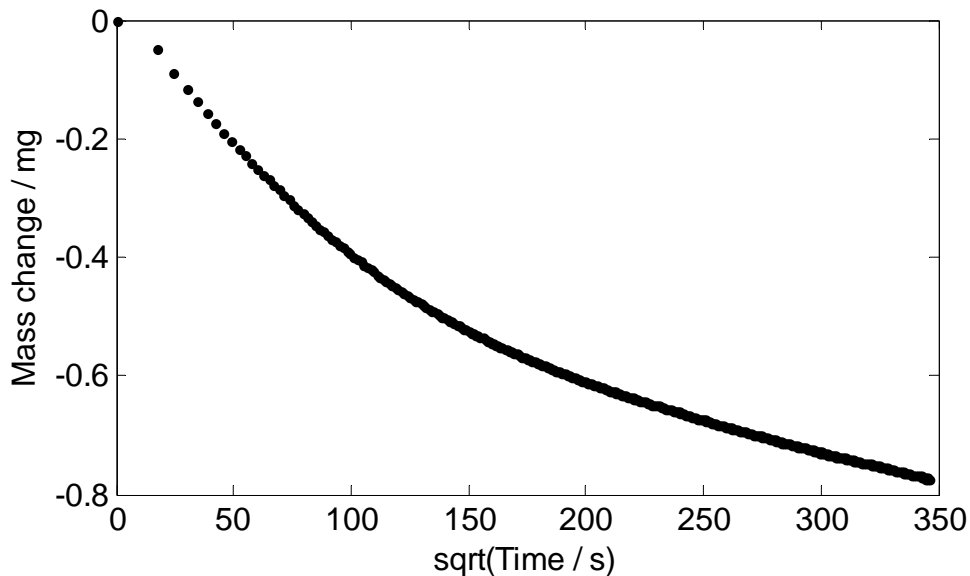

Fig. 2: The mass change as a function of the square root of time for an OPC paste with silica fume (w/c=0.5) undergoing desorption from 60 to 40% RH.

Typically the curves start as looking Fickan, but they do not show the Fickan approach to equilibrium; instead the mass change continues, albeit at a lower and lower rate. We have ruled out that the non-Fickian behavior is caused by limited mass transfer across the surface (boundary layer resistance) or other known limitations of our experimental set-up such as drift of the balance. As the phenomenon is seen in both absorption and desorption, it cannot also be an effect of continued hydration. One other parameter that influences the shape of sorption curves is the transport coefficient's function of the transport potential. However, the changes of the coefficient in such a small RH-interval as 60-40% does not cause more than slight changes to the curve shapes seen in Fig. 1 [3]. A problem with the present measurements is that the initial condition before the step change is not an equilibrium conditions, but more like the conditions at the end of the measurement shown in Fig. 2. However, such non-perfect initial conditions cannot be the cause of the long-term behavior seen in Fig. 2.

It is probable that the non-Fickian behavior is the result of that the sorption that is coupled to the diffusion – the Fickian sorption – is complemented by other much slower local sorption processes. Easily assessable

sorption sites are immediately filled or emptied when the local vapour pressure changes as the result of the macro-diffusion into or out of the sample. Other sorption sites are "hidden" and take a long time to come to equilibrium with the bulk of the material; this gives rise to micro-diffusion on time-scales much longer than those of the macro-diffusion. Non-physical modelling of such behaviour can for example be made with a Fickian sorption complemented by a series of exponential mass uptake terms with different time constants, as has for example been proposed by Berens and Hopfenberg [4]. An example of a possible physical model of the phenomenon is Fickian macro diffusion into the sample coupled to one or more Fickian diffusion processes into less assessable parts of the sample (on a micro-nano level).

Acknowledgements

References

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