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Diffusion of water and methanol vapour in hydrated Portland cement paste

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Diffusion and Adsorption of Water and Methanol Vapor in Hydrated Portland Cement Paste

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Abstract

Equations are developed to describe the combined effect of diffusion and adsorption of water and methanol vapor in hydrated cement paste. The dynamic equation of flow is obtained by equating the space derivative of the spreading pressure of the adsorbed film to a resistive force equal to the product of the coefficient of resistance and the velocity of the film. Qualitative agreement is found for the diffusion of water and methanol vapor through cement paste when the BET and Langmuir equations respectively are used for adsorption. The diffusion of methanol vapor is underestimated due to intercalation and chemical interaction effects. The validity of Fick’s law is discussed.
Introduction

The transport of fluids into microporous media e.g. concrete continues to be a priority area for construction materials research. Sustainable development issues have resulted in a focus on engineering at the micro-scale to extend the service-life of concrete structures\(^1\). Long-term serviceability is of particular importance for the management of hazardous and nuclear wastes\(^2\). Solutions generally involve technology that results in an alteration of the pore structure of cementitious materials in a manner consistent with reduced permeability and diffusivity of fluids and specifically aggressive ions\(^3\).

Modeling of ion and fluid transport in saturated cement systems have been well documented. There is, however, significantly less published information on transport phenomena in partially saturated cement systems. Samson et al. have shown, using an averaging technique, that diffusivity has a contribution from both liquid water and vapor transport\(^4\). The influence of both phases is taken into account through a function \(D_\alpha\) (a non-linear water diffusion coefficient) which contains a term associated to the vapor transport of the liquid phase. Martys has demonstrated that the degree of saturation and the fluids wetting properties are important factors in controlling diffusive transport in porous media\(^5\). It was shown that relative diffusivity can be described by simple polynomial functions. Klinkenberg determined that the permeability of porous media to gas was dependent on the nature of the gas and the pressure\(^6\). He introduced the phenomenon of slip (related to the mean free path of gas molecules) to explain the differences between gas and liquid permeability values. The experiments of Iniya (using concrete materials) have also demonstrated that gas permeability is dependent on water saturation degree\(^7\).

The cases for diffusion in partially saturated cement systems have generally ignored interactions of the fluid with the solid. This is especially true of the adsorbate-adsorbent interaction with vapor phase transport. This will be the focus of this paper. A relationship between water and methanol vapor diffusion in cement systems and the adsorption process will be described. Validation of the arguments will be demonstrated for both BET adsorption isotherms (water vapor) and Langmuir adsorption isotherms (methanol vapor),\(^8,9\). The diffusion of the vapor as a function of the ratio of vapor pressure to saturation vapor pressure will be shown to be consistent with the nature of the sorption isotherm.

Sorption in Hydrated Portland Cement Systems

Water Vapor:

The sorption of water vapor in Portland cement paste is a highly irreversible process\(^10\). Weight change and length change isotherms generally exhibit marked primary and secondary hysteresis (Figure 1). This has been interpreted as due to factors other than adsorption e.g. intercalation of water into the layered structure of C-S-H. The existence of ‘scanning loops’ enable the reconstruction of a ‘reversible’ isotherm (Figure 2) considered necessary for a valid application of the BET theory. Application of adsorption theory requires reversibility in the low humidity ‘adsorption’ region of the isotherm. The ‘reversible’ isotherm will be used to apply the arguments (linking diffusion and adsorption) developed in this paper.
Methanol vapor:
The sorption of methanol vapor in Portland cement paste is very different from that of water vapor\textsuperscript{10,11}. The weight change isotherm is very flat after significant sorption at very low pressures (Figure 3). Strong monolayer binding with little tendency towards multilayer formation is exhibited. This behavior approximates to a Langmuir isotherm. There is however hysteresis like that for water (although much less pronounced). Some interaction between methanol and the C-S-H solids has been shown to take place\textsuperscript{12}. Nevertheless the behavior is assumed to be Langmuir with the monolayer capacity occurring at a partial pressure corresponding to the point of inflection separating adsorption from capillary condensation.

Fluid Flow in Microporous Media

Several authors have reported the results of studies on fluid flow in microporous media\textsuperscript{13,14}. The arguments presented here start with the recognition that three separate conditions must be satisfied in the development of equations for the flow of a homogeneous fluid through microporous media. These conditions are expressed by:

(i) the dynamic equation of motion
(ii) the equation of continuity
(iii) the equation of state

The generalized equation of motion (see Muskat\textsuperscript{15}) in one dimension can be written as follows:

\[
\rho \frac{\partial u}{\partial t} = -\frac{\partial p}{\partial x} + F_x + A_x
\]  
(1)

where, \( t \) is time, \( \rho \) is the fluid density, \( \frac{\partial p}{\partial x} \) is the pressure gradient and \( u \) is the component of velocity, \( F_x \) the component of gravity and \( A_x \) the internal resistance due to friction, all of these quantities in the \( x \) direction. It is assumed that the velocity of flow is small and that all external forces can be neglected. This reduces equation (1) to:

\[
\frac{\partial p}{\partial x} - A_x = 0
\]  
(2)

which states simply that the pressure gradient is balanced by the internal resistance or frictional forces.

Diffusion of a Vapor Through an Adsorbing Medium

The case where a gas is adsorbed on an external surface and migrates through the medium as an adsorbed film on internal surfaces is considered. In the statistical treatment of adsorption (Fowler and Guggenheim\textsuperscript{16}) an adsorbed layer is assumed to have the properties of a two dimensional gas. It is possible to derive a potential function, \( \varphi \), which
has, for an adsorbed film, exactly the same thermodynamic properties that the pressure, \( p \), has for a three dimensional gas. The spreading pressure, \( \varphi \), is related to the free energy of the adsorbed film by the relation:

\[
\varphi = - \frac{\partial F_{\text{ads}}}{\partial A} \tag{3}
\]

where \( F_{\text{ads}} \) is the surface force and \( A \) is the area of the film. The term, \( \varphi \), is a measure of the force that must be applied to keep the film from spreading. The adsorbed film is treated as having a velocity of motion, \( u \), relative to the surface and the resistive force is considered to be proportional to, \( u \). The resistive force is expressed as, \( Cu \) (\( C \) is a constant) and the fundamental dynamic equation is:

\[
\frac{\partial \varphi}{\partial x} + Cu = 0 \tag{4}
\]

where the sign is positive since, \( u \), is in the direction of decreasing pressure.

The following sections describe adsorption behavior for types of adsorption (in cement paste systems) for which a statistical expression of, \( \varphi \), is available.

### Diffusion of Water Vapor in Adsorbing Cement Paste

The BET equation has been applied extensively to hydrated cement systems. The analysis of Cassie and Hill\(^{17,18} \) facilitates the derivation of an expression for the spreading pressure, \( \varphi \), that can be used in this study. The following discussion pertains to how water vapor adsorbed by the BET mechanism would diffuse through hydrated Portland cement paste.

From Hill\(^{18} \), it is noted that the surface force, \( F_{\text{ads}} \) (in equation (3)) can be expressed as:

\[
F_{\text{ads}} = -kT \log Q \tag{5}
\]

where \( Q \) is the complete partition function for BET adsorption. Babbit [19] provides the expression for \( Q \) in terms of the total number of adsorbed molecules, \( N \), the number of localized sites, \( B \), (equivalent to the monolayer capacity), the number of molecules, \( X \), adsorbed on the localized sites and the partition functions, \( j_s e^{\varepsilon_1/kT} \) and \( j_L e^{\varepsilon_L/kT} \) (\( \varepsilon_1 \) is a potential energy in the first layer and \( \varepsilon_L \) is the potential energy in each of the higher layers) for the molecules adsorbed in the first layer and in higher layers respectively.

\[
F_{\text{ads}} = -kT[N \log N + B \log B - (N - X) \log (N - X) - (B - X) \log (B - X) - 2X \log X + X \varepsilon_1/kT + (N - X) \varepsilon_L/kT + X \log j_s + (N - X) \log j_L] \tag{6}
\]

whence

\[
\varphi = -\frac{\partial F_{\text{ads}}}{\partial A} = -\frac{B}{A} \frac{\partial F_{\text{ads}}}{\partial B} = \frac{BkT}{A} \log \frac{B}{B - X} \tag{7}
\]
Substitution of equation (7) into the fundamental dynamic equation (4) gives

\[ u = -\frac{BkT}{CA} \frac{\partial}{\partial x} \left( \log \frac{B}{B-X} \right) \]  

(8)

and the equation for mass transfer becomes:

\[ \text{Nu} = -\frac{kT}{CA} N \frac{B}{B-X} \frac{\partial X}{\partial x} \]  

(9)

The equation given by Cassie\textsuperscript{17} leads to the elimination of X

i.e. \((N - X)(B - X) = \beta X^2\)

where \(\beta = j_L/j_s \exp[(\varepsilon_L - \varepsilon_i)/kT]\)

Thus

\[ \frac{\partial X}{\partial x} = \frac{B - X}{N + B - 2(1-\beta)X} \frac{\partial N}{\partial x} \]

and

\[ X = \frac{N + B \pm \sqrt{(N + B)^2 - 4(1-\beta)NB}}{2(1-\beta)} \]  

(10)

Adopting the minus sign for X (it gives the maximum free energy) and substituting in equation (9) gives:

\[ \text{Nu} = -\frac{kT}{CA} \frac{NB}{\sqrt{(N-B)^2 + 4\beta NB}} \frac{\partial N}{\partial x} \]  

(11)

The classical BET equation can be written as:

\[ \frac{N}{B} = \frac{CP}{(1-P)(1-P+CP)} \]  

(12)

where \(P = p/p_o\) (\(p_o\) is the saturation vapor pressure), \(C = 1/\beta\) and \(N/B = w/V_m\) (the ratio of the amount adsorbed to the monolayer capacity\textsuperscript{20})

Combining equations (11) and (12)

\[ \text{Nu} = -\frac{B^2kT}{CA} \left\{ \frac{1}{\sqrt{1 + \frac{(4\beta - 2)(1-P)(1-P+CP)}{CP}} + \frac{[(1-P)(1-P+CP)]^2}{C^2P^2}} \cdot \frac{C(1-P^2 + CP^2)}{[(1-P)(1-P+CP)]^2} \frac{\partial P}{\partial x} \right\} \]  

(13)
Results of adsorption experiments generally obey the following equation for mass transfer

\[ \text{Nu} = -D_p \frac{\partial P}{\partial x} \]  \hspace{1cm} (14)

Combining equations (13) and (14) gives

\[ D_p = \frac{B^2 kT}{CA} \psi \]  \hspace{1cm} (15)

where \( \psi \) represents the expression in brackets in equation (13). It is apparent from equations (14) and (15) that the diffusion coefficient of cement paste or other microporous solids should vary with pressure if adsorption follows the BET isotherm and the assumptions used in developing this argument are correct. Equation (13) is generally integrated before it is applied.

Equation (11) (mass transfer) can be written in the form

\[ \text{Nu} = -\frac{B kT}{CA} \frac{N}{\sqrt{Y}} \frac{\partial N}{\partial x} \]  \hspace{1cm} (16)

where \( Y = (N - B)^2 + 4\beta NB \) \hspace{1cm} (17)

Equation (16) is equivalent to

\[ \text{Nu} = -\frac{B kT}{CA} \frac{\partial}{\partial x} \left[ \sqrt{Y} - B(2\beta - 1) \log \left[ \sqrt{Y} + N + B(2\beta - 1) \right] \right] \]  \hspace{1cm} (18)

and using the equation of continuity in the form \( \frac{\partial (\text{Nu})}{\partial x} = -\frac{\partial N}{\partial t} \)

we obtain the equation

\[ \frac{\partial N}{\partial t} = \frac{B kT}{CA} \frac{\partial^2}{\partial x^2} \left[ \sqrt{Y} - B(2\beta - 1) \log \left[ \sqrt{Y} + N + B(2\beta - 1) \right] \right] \]  \hspace{1cm} (19)

The movement of water vapor through the porous solid (considered as an adsorbing membrane - e.g. cement paste) from the surface at \( x = 0 \) where \( P = P_o \) to the surface at \( x = L \) where \( P = P_L \) is considered.
Integration of equation (18) gives:

\[ \text{Nu} = \frac{B k T}{\text{CA} \ L} \left( \sqrt{Y} - B(2\beta - 1) \log \left[ \sqrt{Y} + N + B(2\beta - 1) \right] \right)_{N=N_L}^{N=N_o} \] (20)

Also integration of equation (14) gives:

\[ \text{Nu} = \frac{D_p P_o - P_L}{L} \] (21)

Equating equations (20) and (21) gives an expression for the diffusion coefficient, \( D_p \):

\[ D_p = \frac{B k T}{\text{CA} \ L} \left( \sqrt{Y} - B(2\beta - 1) \log \left[ \sqrt{Y} + N + B(2\beta - 1) \right] \right)_{N=N_L}^{N=N_o} \] (22)

Substituting for \( Y \) (equation (17)) and using the BET equation to change the independent variable from \( N \) to \( P \), an expression is obtained for \( D_p \) as a function of pressure.

\[ D_p = \frac{B^2 k T}{\text{CA} \ P_o - P_L} \left\{ \sqrt[4]{\frac{C^2 P^2}{[(1-P)(1-P+CP)]^2} + \frac{(4\beta - 2)CP}{(1-P)(1-P+CP)} + 1} - 2(\beta - 1) \log \left[ B \sqrt[4]{\frac{C^2 P^2}{[(1-P)(1-P+CP)]^2} + \frac{(4\beta - 2)CP}{(1-P)(1-P+CP)} + 1} \right] \right\}_{P=P_o}^{P=p} + \frac{BCP}{(1-P)(1-P+CP)} + B(2\beta - 1) \right\}_{P=P_o}^{P=p} \] (23)

Simplifying by denoting

\[ Y = \frac{C^2 P^2}{[(1-P)(1-P+CP)]^2} + \frac{4(\beta - 2)CP}{(1-P)(1-P+CP)} + 1 \]

gives

\[ D_p = \frac{B^2 k T}{\text{CA} \ P_o - P_L} \left\{ \sqrt{Y_o} - \sqrt{Y_L} \right\} \left\{ \sqrt[4]{\frac{Y_o}{(1-P_o)(1-P_o+CP_o)} + \frac{BCP_o}{(1-P_o)(1-P_o+CP_o)} + B(2\beta - 1)} - (\beta - 1) \log \left[ \sqrt[4]{\frac{Y_L}{(1-P_L)(1-P_L+CP_L)} + \frac{BCP_L}{(1-P_L)(1-P_L+CP_L)} + B(2\beta - 1)} \right] \right\} \] (24)

where \( Y_o \) and \( Y_L \) are values of \( Y \) at \( x=0 \) and \( x=L \).
The Diffusion Constant, $D_p$, versus Relative Humidity

The ratio $D_p/[B^2 kT/CA]$ given by equation (24) can (to a first approximation) be plotted as a function of $P$ (relative humidity) for hydrated cement paste (Figure 4) where $P_o = P$ and $P_I$ is taken as zero. Values of $\beta$, $B$ and $C$ (0.093, 1.140 and 11.0 respectively) were determined from a BET analysis of the ‘reversible’ sorption isotherm for cement paste, w/c = 0.50 and used to calculate the bracketed quantity in equation (24). The curve for the ratio in Figure 4 exhibits a sinusoidal shape similar to that observed for the ‘reversible’ weight change isotherm (also shown in the figure). Each curve has a rise in the value of the ordinate at low humidity and reverses curvature forming a ‘knee’ at about 10% relative humidity. This is followed by an approximately linear increase in weight up to about 40% relative humidity and a much larger exponential increase at higher humidities (due to capillary condensation effects) typical of a BET adsorption mechanism. The curve for diffusion at high humidities is a prominent characteristic of diffusion through adsorbing solids such as cement paste. It is noted that the BET equation is strictly applicable only in the adsorption region of the isotherm, i.e. below 40% relative humidity. The BET equation does indicate however, the large increase of adsorption (for cement paste) that is characteristic of the adsorption of water vapor as saturation is approached. The equation therefore can be considered as giving a qualitative indication of the behavior at high humidities. It is important to note that it can be inferred from the results for cement paste (in equilibrium with water vapor) that where there is an interaction between the diffusing gas (in this case, water vapor) and the solid the use of Fick’s law as a fundamental equation of diffusion is not valid. This derives from the fact that pressure gradients are not linearly related to concentration gradients. It is important to note that the pressure (and its analogous quantity $\varphi$) is the potential whose space derivative gives the force that is balanced by the resistive forces. As stated above a Fick’s law approach is correct only when the concentration is directly proportional to the pressure. The flux associated with the dynamic equation in an adsorbing medium is proportional to the velocity of flow and not to the concentration gradient. A thermodynamic argument pertaining to the validity of Fick’s law is given in Appendix 1.

Diffusion of Methanol in an Adsorbing Cement Paste

The sorption isotherm for methanol as an adsorbate in cement paste (Figure 3) has the characteristics of a Langmuir isotherm. The Langmuir isotherm is based on a model of a localized monolayer. Adsorption can be expressed in the form

$$\theta = \frac{\alpha P}{1 + \alpha P}$$  \hspace{1cm} (25)

where $\theta$ is the fraction of sites occupied and $P$ is the ratio of the vapor pressure to the saturation vapor pressure. $\alpha$ is a constant. Fowler and Guggenheim have obtained the following expression for spreading pressure\textsuperscript{16}.

$$\varphi = \frac{N_s kT}{A} \log \frac{1}{1 - \theta}$$  \hspace{1cm} (26)
Substitution of equation (26) into the fundamental dynamic equation (4) gives:

\[ \frac{N_s k T}{A} \frac{\partial}{\partial x} \left( \log \frac{1}{1 - 0} \right) + C u = 0 \]  \hspace{1cm} (27)

Rearranging equation (27) with \( \theta = N/N_s \) \( \text{(N=number of adsorbed molecules)} \) gives:

\[ u = -\frac{N_s k T}{C A} \frac{\partial}{\partial x} \left( \log \frac{N_s}{N_s - N} \right) \]  \hspace{1cm} (28)

The equation of mass transfer is written as:

\[ \text{Nu} = -\frac{N_s k T}{C A} N \frac{\partial}{\partial x} \left( \log \frac{N_s}{N_s - N} \right) \]  \hspace{1cm} (29)

The equation of continuity as previously expressed is:

\[ \frac{\partial (\text{Nu})}{\partial x} = -\frac{\partial N}{\partial t} \]

Introducing equation (28) leads to:

\[ \frac{\partial N}{\partial t} = \frac{N_s k T}{C A} \frac{\partial}{\partial x} \left( \frac{N}{N_s - N} \frac{\partial N}{\partial x} \right) = \frac{N_s k T}{C A} \frac{\partial^2}{\partial x^2} \left[ N_s - N - N_s \log(N_s - N) \right] \]  \hspace{1cm} (30)

This is the differential equation for diffusion in an adsorbing solid when adsorption obeys the Langmuir isotherm.

The rate of diffusion of a gas through a solid can be determined by measuring the mass transferred through its thickness under a constant pressure difference.

The equation for mass transfer can be expressed as:

\[ \text{Nu} = -\frac{N_s k T}{C A} \frac{\partial}{\partial x} \left[ N_s - N - N_s \log(N_s - N) \right] \]  \hspace{1cm} (31)

Integrating from \( x = 0 \) to \( x = L \) gives:

\[ \text{Nu} = \frac{N_s k T}{C A} \frac{1}{L} \left[ N_s - N - N_s \log(N_s - N) \right] \right|_{N_s = N_s}^{N_s = 0} \]

\[ = -\frac{N_s k T}{C A} \frac{1}{L} \left[ N_o - N_L + N_s \log \frac{N_s - N_o}{N_s - N_L} \right] \]  \hspace{1cm} (32)
or expressing equation (32) in terms of $\theta = N/N_s$

$$\text{Nu} = -\frac{N^2 \kappa T}{CA} \frac{1}{L} \left[ \theta_o - \theta_L + \log \frac{1 - \theta_o}{1 - \theta_L} \right]$$

Equation (33) gives the amount of gas diffusing through the cement paste when $\theta = \theta_o$ on one surface and $\theta = \theta_L$ on the other. To test the equations for methanol adsorption on cement paste, it is assumed that the partial pressure at $x = L$ is 0 and hence $\theta_L = 0$. The results of Mikhail$^{11}$ for methanol adsorption in cement paste ($w/c = 0.35$) are used for the calculations. The monolayer capacity, $\theta_m$, is taken as 0.02 g/g. This occurs at a value of $P$ of about 0.45 (the point of inflection marking the onset of capillary condensation). The ratio $\text{Nu}/(\text{Nu})_{P=0.45}$ is plotted against the partial pressure (Figure 5). This ratio is a measure of the mass fraction of that diffusing at the reference pressure. Curves for surface coverage, $\theta$, and the Langmuir equation (25) ($\alpha = 12$) are also plotted. The similarity of the first two curves support the assumption that the adsorption of methanol on cement paste can be described as Langmuir adsorption. The coverage is however underestimated by the estimates of the ratio $\text{Nu}/(\text{Nu})_{P=0.45}$. This may be due to interactions other than adsorption of methanol with the cement paste solids (C-S-H)$^{21}$. It has been reported that methanol molecules may to some extent intercalate between the C-S-H sheets. A chemical reaction with the C-S-H phase has also been detected.

**Conclusions**

1. The adsorbate-adsorbent interaction is shown to be an important factor governing the diffusion of vapor in hydrated Portland cement systems.
2. Diffusion of water vapor in hydrated cement systems obeying the BET isotherm can be described using a fundamental dynamic equation expressed in terms of the spreading pressure of an adsorbate film.
3. Coupling of adsorption and diffusion phenomena associated with water vapor transport in cement pastes and application of the BET theory to water sorption isotherms requires the construction of a ‘reversible’ isotherm to avoid issues related to intercalation effects.
4. The diffusion coefficient for transport of water vapor through microporous cement paste is shown to be dependent on the relative humidity. The dependence has the same form as the ‘reversible’ water isotherm for cement paste.
5. The use of Fick’s law as the fundamental equation of diffusion would appear to be invalid when there is an interaction between the diffusing gas and the solid (C-S-H).
6. Diffusion of methanol obeying the Langmuir isotherm in hydrated cement systems can be described using a fundamental dynamic equation for the diffusion of an ideal localized monolayer expressed in terms of the spreading pressure of the adsorbate film. Intercalation and chemical interaction effects generally result in an underestimation of the monolayer surface coverage.
References


Appendix 1

The validity of Fick’s law to model diffusion of vapor in microporous materials subject to adsorbate-adsorbent interactions is discussed as follows. Consider Einstein’s treatment for diffusion,

\[ J_i = -X_i B_i \frac{\partial \Delta G_i}{\partial l} \]

where \( X_i \) is concentration, \( B_i \) is mobility and the derivative is the gradient of the partial molar free energy over the distance, “\( l \”).

Recall,

\[ \Delta G_i = \mu_i - \mu_i^o = RT \ln a_i = RT \ln X_i + RT \ln \gamma_i \]

where \( \mu_i \) is the chemical potential, \( \mu_i^o \) is the standard chemical potential, \( a_i \) is the activity, \( X_i \) is concentration and \( \gamma_i \) is the activity coefficient. Substituting \( \Delta G_i \) into the flux equation gives,

\[ J_i = -X_i B_i RT \left[ \frac{\partial \ln X_i}{\partial l} + \frac{\partial \ln \gamma_i}{\partial l} \right] \]

But,

\[ \frac{\partial \ln X_i}{\partial l} = \frac{1}{X_i} \frac{\partial X_i}{\partial l} \]

So,

\[ J_i = -X_i B_i RT \left[ \frac{1}{X_i} \frac{\partial X_i}{\partial l} + \frac{\partial \ln \gamma_i}{\partial l} \right] \]
Since \( \frac{X_i}{X_i} = 1 \), we can write

\[
J_i = -X_i B_i RT \left[ \frac{1}{X_i} \frac{\partial X_i}{\partial t} + \left( \frac{X_i}{X_i} \right) \frac{\partial \ln \gamma_i}{\partial t} \right]
\]

Or,

\[
J_i = -B_i RT \left[ \frac{\partial X_i}{\partial t} + X_i \frac{\partial \ln \gamma_i}{\partial t} \right]
\]

Factoring out \( \frac{\partial X_i}{\partial t} \) gives,

\[
J_i = -B_i RT \left[ 1 + X_i \frac{\partial \ln \gamma_i}{\partial X_i} \right] \left( \frac{\partial X_i}{\partial t} \right)
\]

Now, compare this expression for flux with the typical, classic Fick’s law

\[
J_i = -D \left( \frac{\partial X_i}{\partial t} \right)
\]

Therefore,

\[
D = B_i RT \left[ 1 + X_i \frac{\partial \ln \gamma_i}{\partial X_i} \right]
\]

In the “ideal” case, \( \gamma_i = 1 \), so

\[
D = B_i RT
\]

In the case of adsorption etc., \( \gamma_i \neq 1 \) (i.e. non-ideal conditions, non-ideal gas, etc.)

This shows that Fick’s law only really works in ideal cases where the activity of the species is the concentration. When gas is absorbed, it is not valid to use the ideal Fick’s law. Furthermore, diffusion of gas into cement paste is somewhat similar to hydrogen diffusion into mild steel\(^{22}\). This work showed that the traditional Fick’s Law fails because hydrogen is trapped in the lattice imperfections (analogous to intercalates in the C-S-H structure).
Figure 1. Weight change (a) and length change (b) scanning isotherms of Portland cement paste (w/c = 0.50), (Ref. [10])

Figure 2. Constructed “reversible” weight change water isotherm for Portland cement paste (w/c = 0.50), (Ref. [10])
Figure 3. Weight change isotherm of methanol on hydrated Portland cement paste (w/c = 0.50), (Ref. [10])

Figure 4. Diffusion ratio and “reversible” sorption isotherm for hydrated cement paste
Figure 5. Adsorption of methanol vapor on hydrated cement paste (w/c = 0.35)