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FLR technique Exchange kinetics of ethanol/fluorescent dye with water in water-saturated cement paste examined by ^{1}H- and ^{2}H-NMR

Eddy W. Hansen[a,]*, Hans. Chr. Gran[b]

[a]Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo, Norway
[b]Norwegian Building Research Institute, P.O. Box 123, Blindern, 0314 Oslo, Norway

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Abstract

A water-saturated cement paste (water-to-cement, w/c=1.0) confined in a solution of ethanol saturated with a fluorescent dye showed complete exchange of water after 2 days. The exchange rates of water and ethanol were independent of the presence of dye and determined to be 42×10^{-8} and 60×10^{-8} cm^2/s, respectively. The exchange rate of dye was significantly smaller, by a factor of two to three. The exchange process resulted in a partitioning of the concentration of dye in ethanol within cement and bulk of (0.46+0.20). ^{1}H-NMR spectral analysis of the dye before and after exchange suggests the dye to be inert, i.e., it does not react with the cement paste. Furthermore, no indication of a reaction between ethanol and cement paste is observed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cement paste; Pore solution; Diffusion; Spectroscopy; Exchange

1. Introduction

An impregnation technique based on a fluorescent dye dissolved in an alcohol has been proposed [1] and makes it possible to do plane section and thin section analysis on concrete of very low water-to-cement (w/c) ratio. The technique is called fluorescent liquid replacement (FLR) and is based on a principle where the pore water is slowly replaced by an alcohol/fluorescent dye solution. Compared to traditional epoxy impregnation the technique is shown to provide a significant increase in impregnation capability in concrete. The risk of introducing cracks and damage to the pore structure during impregnation is greatly reduced.

Of particular importance is the time needed for exchange of water (within the water-saturated cement paste) with the alcohol solution. This exchange process has been investigated in situ, by monitoring ^{1}H- and ^{13}C-NMR spectra of exchanging ethanol with water as a function of process time [2,3]. However, one subject not being addressed in the previous studies concerns the fate of the fluorescent dye during the exchange process. Will the exchange rate of dye between bulk ethanol and cement paste be different from the exchange rate of ethanol? For instance, the diffusivity of the fluorescent dye may be smaller than the diffusivity of the alcohol due to differences in molecular size (or molecular weight). Also, the cement paste may behave as a sort of chromatographic substance, which changes this concentration. Another parameter of significance is the relative solubility of dye in water and ethanol, respectively. Differences in solubility may lead to changes in the relative amount of dye and alcohol within the cement paste both in time and space. Of particular importance is whether the dye is inert or if it may react with the inner/outer surface of the cement paste.

Recent ^{1}H-NMR studies [4] suggest that in a system composed of cement paste–water–methanol/dye, one or both of the latter two species react with the cement paste. In this work, ^{1}H- and ^{2}H-NMR spectroscopy will be applied to investigate the exchange of ethanol/dye with water in a water-saturated cement paste having a w/c ratio of 1.0. Since ethanol (rather than methanol) is used as an exchange fluid in the FLR technique, it is of importance to establish whether ethanol is chemically inert or not. This question will also be addressed in this work.

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* Corresponding author. Tel.: +47-2-285-5692; fax: +47-2-285-5446.
E-mail address: eddywh@kjemi.uio.no (E.W. Hansen).

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2. Experimental

2.1. Specimen

Samples of hydrated cement paste (HCP) with a w/c ratio 1.0 were prepared from a Danish Super White Portland Cement certified as a British Standards Institution class 62.5N cement. The Bogue composition was 65.8% tricalcium silicate (C_3S), 21.0% dicalcium silicate (C_2S), 4.2% tricalcium aluminate (C_3A), 1.0% tetracalcium alumina ferrite (C_4AF), and 2.3% calcium oxide (C). The Blaine surface was 4000 cm^2/g. The reason for using a white cement was its low content of paramagnetic constituents, like Fe_2O_3 and Mn_2O_3, that may contribute to the NMR relaxation [5]. The composition by weight of the cement was determined by X-ray fluorescence spectroscopy. The paste was mixed under slight vacuum (0.1 bar) to avoid entrapped air and molded and sealed in cylindrical polytetrafluoroethane forms with diameter of 20 mm and length of 120 mm. The total weight of the mixture was checked before and after mixing to detect any loss of water resulting from the vacuum treatment. The paste was slowly rotated during the first 20 h of hardening to avoid separation between water and cement. After demolding, the paste was stored in water at room temperature. The sample was 3 months old at the time of testing, and was cut from the interior of the molded cylinders to avoid possible inhomogeneities in the paste caused by the proximity to the form walls.

The sample of HCP was cut and ground to a diameter of approximately 3.76 mm and length of 5–15 mm to fit into the NMR tube. The sample was stored in 99.8% deuterated water (Aldrich, 15188-2 and denoted ethanol-d6 in this work) for half a year before measurements were initiated. The replacement of normal water with deuterated water was applied in order to reduce the strong background signal from normal water. Without this step, the water signal might mask the much weaker signal from the fluorescent dye, which may become unobservable due to dynamic range limitations [6]. Of similar reasons, the ethanol used was of 99.8% isotopic purity (Aldrich, 18641-4), denoted ethanol (d6).

The ethanol solution was saturated with a fluorescent dye of unknown structure, molecular weight and ele– ment composition.

The water-saturated cement paste was inserted into a large reservoir of dye saturated ethanol (5.0 g) and taken out at specific times during the exchange process for NMR measurements. Immediately before testing, fluid on the external surface was wiped away with an absorbent tissue before the specimen was transferred to a 5-mm NMR tube.

2.2. NMR

The ^{1}H- and ^{2}H-NMR spectra were acquired on a Varian VXR 300 NMR spectrometer, operating at 300 MHz proton resonance frequency, using a high-resolution 5-mm probehead. The number of transients was set to 16 (proton). A radio frequency (rf) pulse of 90° tip-angle and a repetition time between rf pulses of 30 s were used in both types of experiments. The repetition time was set to five times the longest T_1 for both the deuterium and proton nuclei. The sweep width was set to cover 25 kHz.

In order to acquire quantitative spectra, the spin–lattice relaxation time (T_1) was determined by applying a conventional inversion recovery (180°–τ–90°) pulse sequence [6]. The spin–lattice relaxation times of the different resonance lines of the dye molecule were all in the range of 0.5–1.5 s. The T_1 of the residual methylene proton peak and the residual OH peak of deuterated ethanol were 5.8 and 8.2±0.3 s, respectively.

3. Results and discussion

A key object of this work is to monitor the concentration of dye in ethanol within the cement paste as a function of exchange time. However, the relatively small amount of fluorescent dye in the solution combined with severe line broadening (due to susceptibility difference between the

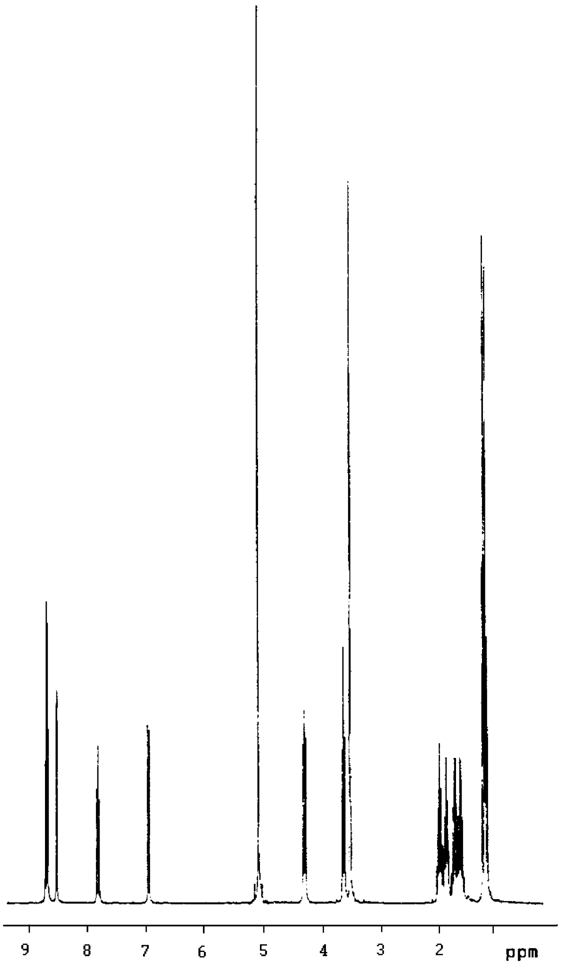

Fig. 1. ^{1}H-NMR spectrum of ethanol-d6 saturated with fluorescent dye. Nonmarked peaks belong to the dye molecule.

confined fluid and the solid cement matrix), made it difficult—if not impossible—to identify the signal of fluorescent dye within the cement paste. The concentration of dye in ethanol within the cement paste can therefore only be monitored indirectly, by observing the NMR signal intensity in the liquid phase surrounding the cement paste during an exchange process. This will be discussed in a later section.

The ^{1}H-NMR spectrum of a bulk ethanol solution saturated with a fluorescent dye is shown in Fig. 1. To enable the exchange process to be monitored as a function of reaction time, a number of identical samples were prepared and inserted into solutions having the same reactant concentrations. Each cement sample was taken out of its respective solution at successive times during the exchange process and the solutions analyzed separately. All samples showed pore volumes in the range of 0.444±0.014 ml/g. The deuteron spin–lattice relaxation times of the water (D_2O) within the different cement pastes were—within experimental error—the same [$T_{1,\text{average}}$=10.7±0.1 ms], suggesting the pore size distribution of the different samples to be identical.

3.1. Quantitative ^{2}H-NMR

The quantitative applicability of ^{1}H-NMR spectroscopy of water confined in cement pastes has previously been established [2]. Due to the variable dimension of the cement pastes (5–15 mm in height) investigated in this work, a quantitative evaluation of the ^{2}H-NMR technique is made possible. The results are depicted in Fig. 2, showing a linear relation between the observed signal intensity and the amount of deuterated water within the cement pastes. The relative uncertainty was estimated to be less that 5%.

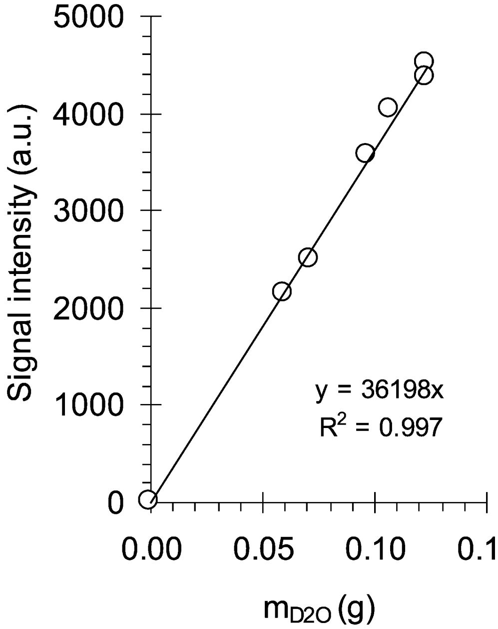

Fig. 2. ^{2}H-NMR signal intensity as a function of the amount ($m_{D_2}O$) of deuterated water within completely water-saturated cement pastes. The solid curve represents a constrained linear least square fit to the data (forced to go through 0.0).

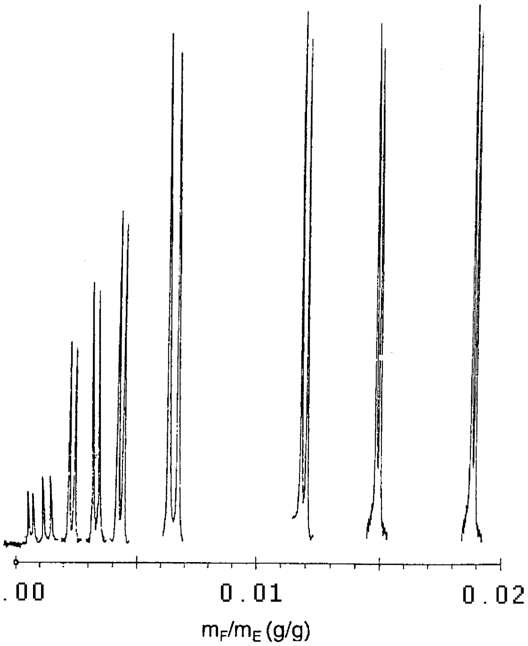

Fig. 3. ^{1}H-NMR spectra of dye (only resonance peak δ=6.95 ppm is shown) as a function of the relative amount (m_F/m_E) of dye (F) in ethanol (E). From left to right: m_F/m_E=0, 6.940×10^{-4}, 1.243×10^{-3}, $2{,}295\times10^{-3}$, 3.293×10^{-3}, 4.315×10^{-3}, 7.016×10^{-3}, 1.206×10^{-3}, 1.476×10^{-3}, 1.911×10^{-3}.

3.2. Solubility of fluorescent dye in ethanol and water

Ten different solutions of fluorescent dye (F) dissolved in ethanol (E) were prepared. The ^{1}H-NMR spectra of one of the dye peaks (δ=6.95 ppm; Fig. 1) are shown in Fig. 3 as a function of the relative mass ratio m_F/m_E. The same change in peak intensity as a function of m_F/m_E is found for all other resonance peaks of the dye molecule in Fig. 1. Fig. 4 shows the ratio of the signal intensity (I_F) of the dye peak (δ=6.95 ppm) and the signal intensity (I_E) of the ethanol peak (δ=3.4 ppm), i.e., I_F/I_E, as function of the mass ratio m_F/m_E. For mass ratios $m_F/m_E \geq 0.01$ g/g, the signal intensity ratio becomes constant, suggesting that a solubility limit of dye in ethanol is reached. This statement is supported by the formation of a precipitate, as observed by visual inspection of the three latter solutions. The intersection of the two straight lines in Fig. 4 defines the solubility limit of dye in ethanol and amounts to 7.01±0.16 g dye/g ethanol. For comparison, the solubility of dye in methanol (on a molar basis) is six times larger than in ethanol [4].

Since the exchange process investigated in this work involves not only dye/ethanol but also water, it is of importance to estimate the solubility of dye in a water/ethanol solution as well. Adding water to a saturated dye/ethanol solution and performing the same type of NMR analysis as

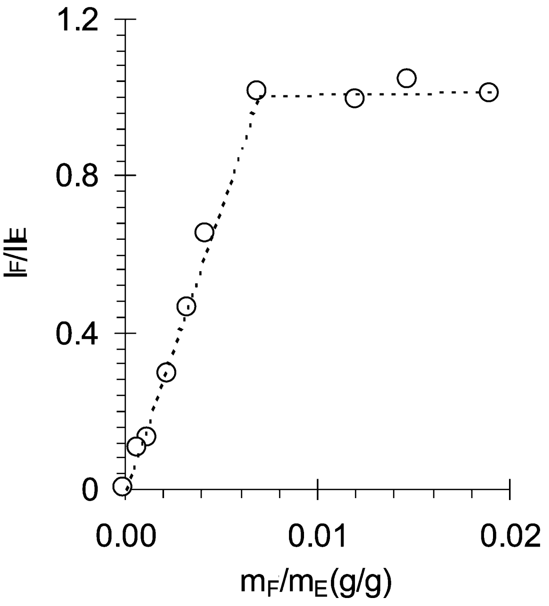

Fig. 4. Signal intensity ratio I_F/I_E of dye (F) and ethanol (E) as a function of the mass ratio (m_F/m_E) between the two species. The dotted curves represent linear least square fits. The intersection between the two lines defines the solubility of dye in ethanol.

just outlined, the solubility of dye in ethanol/water can be determined. The results are summarized in Fig. 5 and suggest that when dye/ethanol diffuse into the water-saturated cement paste, dye will probably precipitate out at the interface between water and ethanol and subsequently dissolve as additional ethanol enters the cement paste. However, if the volume of the dye/ethanol solution (the reservoir) is significantly larger than the pore volume of the cement paste, the cement paste will be completely saturated with ethanol/dye after the exchange process has reached an equilibrium state. This will be the situation discussed in the next section.

3.3. Exchange of water (D_2O) with fluorescent dye/ethanol

Two identical, water (D_2O)-saturated cement pastes with volumes of 0.12 ml were inserted into large reservoirs (25 ml) of ethanol (System A) and ethanol saturated with a fluorescent dye (System B), respectively. The ethanol used was nondeuterated and denoted ethanol-h6 (to distinguish it from deuterated ethanol, ethanol-d6). The cement samples were taken out of their ethanol solutions at certain times during the exchange process and NMR spectra (^{1}H- and ^{2}H-NMR) acquired before the samples were replaced into their respective reservoirs for subsequent measurements. The ^{1}H- and ^{2}H-NMR spectra of one of the cement pastes (System A) are shown as a function of exchange time in Fig. 6.

The ^{2}H-NMR signal intensities of D_2O within the two cement pastes (Systems A and B) as a function of exchange time are plotted in Fig. 7A and reveal the same time behavior. Likewise, the ^{1}H-NMR signal intensities of ethanol within the two cement pastes as a function of exchange time (Fig. 7B) are—within experimental error—the same.

3.4. Exchange rates derived from NMR measurements

To derive a mathematical expression for the exchange rate or diffusivity of a fluid moving into or out of a porous material it is of some concern to establish whether the diffusion process is Fickian or not. It has recently been reported [2,3] that diffusion of ethanol into virgin and preheated HCPs with w/c ratio of 0.3:1.0 could be fitted to Fick's second law. Ritger et al. [7] introduced a simple exponential relation:

$$\frac{I_t}{I_0} = kt^N. \tag{1}$$

To describe the general solute release behavior of controlled-release polymer devices, where I_t/I_0 is the fractional solute release, t is the release time, k is constant, and N is the diffusional exponent characteristic of the release mechanism. If considering a fluid diffusing out of a porous material, Eq. (1) can be modified to read:

$$\frac{I_0 - I_t}{I_0} = kt^N \tag{2}$$

where I_t/I_0 now describes the fractional amount of fluid remaining within the porous material at time t. It is evident that Eqs. (1) and (2) are valid only when the left side of these equations are less than a certain limiting value, denoted by F_c. Ritger et al. [7] have shown that in the case of pure Fickian diffusion, the exponent N has a limiting value of 0.46 for diffusion into a cylinder of infinite length.

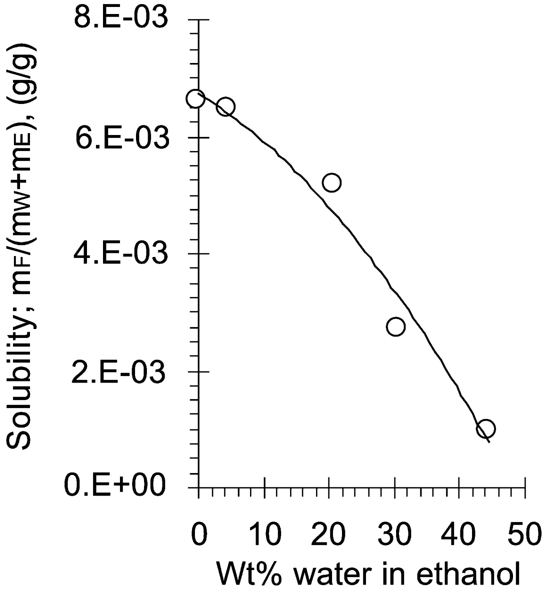

Fig. 5. Solubility of fluorescent dye in ethanol/water as a function of the wt.% water. The solubility is expressed as amount of dye dissolved in the amount of ethanol+water (g/g). The solid curve represents a simple exponential fit and has no theoretical relevance.

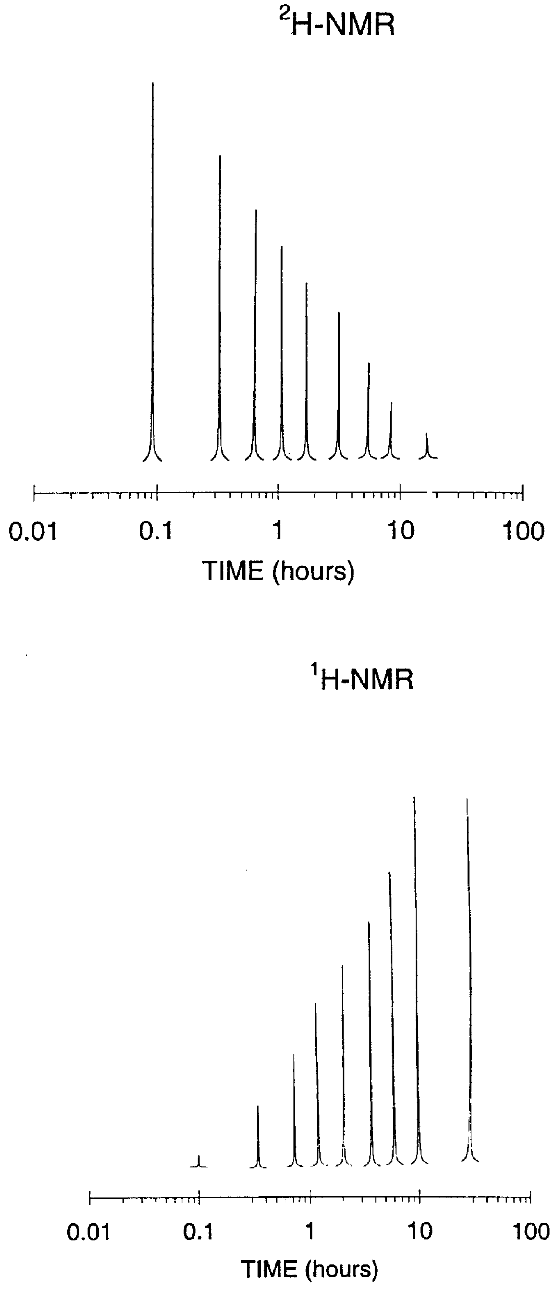

Fig. 6. ^{1}H- and ^{2}H-NMR spectra of water (A) and ethanol (B) in a cement paste as a function of time during exchange of water (D_2O) with ethanol-h6. The water-saturated cement paste is placed in a reservoir of ethanol-h6.

Depending on the ratio of length to the diameter of the sample (the aspect ratio), Fickian diffusion mechanism is described by N having a value within the range of approximately 0.40–0.50. We have fitted Eqs. (1) and (2) to the data in Fig. 7A and B for $b<0.6$. The derived exponents N are tabulated in Table 1 and show that for ethanol diffusing into the cement paste, N (=N(1) in Table 1) satisfies the above criterion for Fickian diffusion. This is in agreement with the results obtained by Feldman [8] from gravimetric measurements on replacement of water by propan-2-ol and methanol in HCP. Feldman [8] found a linear behavior between the amount of water being replaced as a function of the square root of reaction time.

For water diffusing out of the cement pastes, the exponents N (=N(2) in Table 2) are slightly smaller and somewhat outside the actual region defining pure Fickian diffusion. The exact reason for this discrepancy is not understood. However, in spite of this difference, we have treated all diffusion/exchange processes as Fickian, enabling the Fick's second law to be applied, which in cylindrical coordinates can be written [9] (Eq. (3)):

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right] \tag{3}$$

where D is the diffusion coefficient and r is the distance from the center of the cylindrical sample. C is the concentration of the specie at time t and a distance r from the center of the cylinder. Since the cylindrical cement samples are confined in an infinite reservoir of ethanol/dye, the boundary conditions can be written:

$$C(r = a, t = 0) = C_0 \tag{4a}$$

where C_0 is the (constant) concentration of ethanol(/dye) at the cement/ethanol interface at any time t. The initial condition satisfies Eq. (4b):

$$C(r, t = 0) = 0 \tag{4b}$$

since the sample is initially saturated with water (D_2O) and thus contains no ethanol/dye. Eq. (4a), together with the specified boundary (Eq. (4a)) and initial (Eq. (4b)) conditions, can be solved by invoking a Laplace transform technique. This approach has been detailed elsewhere [9], so only the main result will be presented here, Eq. (5):

$$\frac{I_t}{I_0} = \left[1 - \beta\sum_{n=1}^{\infty}\frac{1}{\alpha_n^2}\exp\left(-\alpha_n^2 D\frac{t}{a^2}\right)\right] \tag{5}$$

where the parameter β is equal to 4 for $n=\infty$. The terms α_n are the positive roots of $J_0(a\alpha_n)=0$, where J_0 is the zero-order Bessel function of the first kind. Eq. (5) converges slowly so it is necessary to use a large number of terms. We have chosen eight terms and used a value of β equal to 4.207, which is slightly different from the theoretical value of 4. This value of β was used to force I_t/I_0 to be equal to 0 for $t=0$. The eight α_n values used are $\alpha_1=2.405$, $\alpha_2=5.520$, $\alpha_3=8.654$, $\alpha_4=11.79$, $\alpha_5=14.93$, $\alpha_6=18.07$, $\alpha_7=21.21$, and $\alpha_8=24.35$. Thus, two adjustable parameters, D and I_0, are involved in the curve fitting.

The solid curves in Fig. 7 represent nonlinear least square fits to Eq. (5). The derived diffusion coefficients (D) or exchange rates are shown in Table 2, and show that the diffusion of water (D_2O) out of the cement paste is independent of the presence of dye within the ethanol reservoir. Based on statistical arguments (95% confidence interval) we conclude that the diffusion of ethanol into the cement paste is independent of the presence of dye as well.

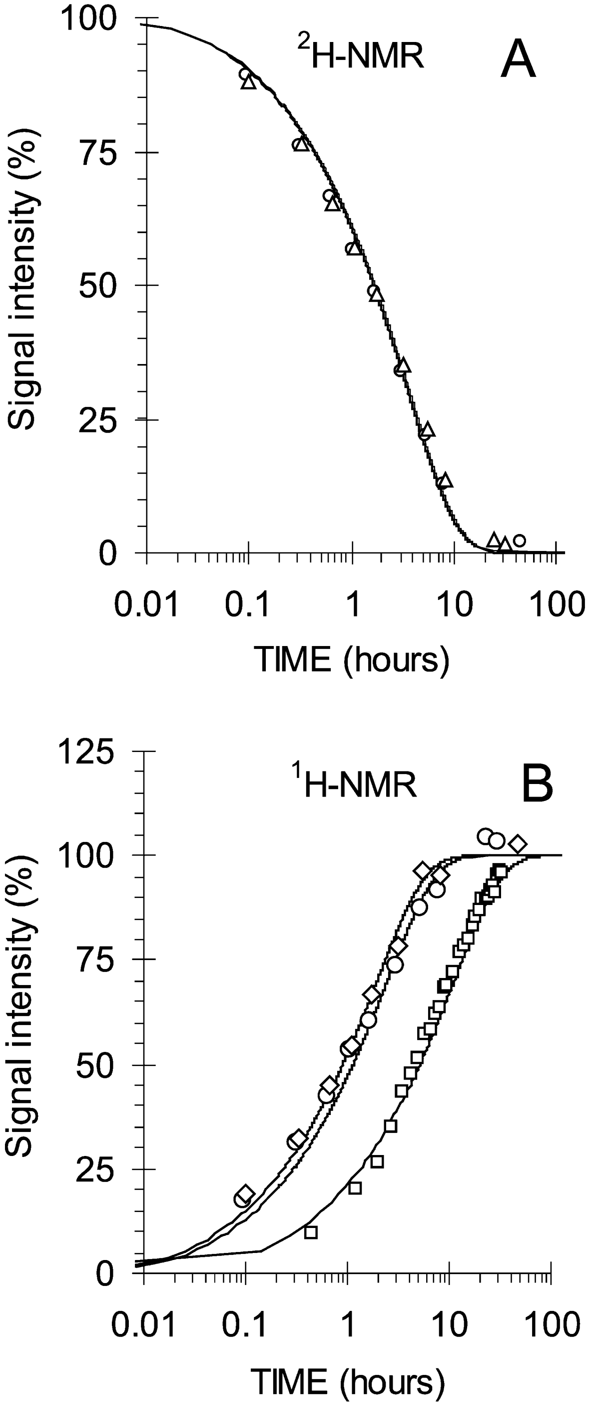

Fig. 7. (A) ^{2}H-NMR signal intensity of water (D_2O) within a cement paste during exchange with ethanol-h6 (○) and dye/ethanol-h6 (◇) as a function of exchange time. (B) ^{1}H-NMR signal intensity of ethanol-h6 (○) and ethanol-h6 (◇)/dye within a cement paste during exchange with water (D_2O) as a function of exchange time. The open squares (□) represent the ^{1}H-NMR signal intensity of fluorescent dye in an ethanol-d6 solution surrounding a cement paste as a function of exchange time. The cement paste was initially saturated with dye/ethanol-d6. The surrounding ethanol-d6 solution initially contained no dye.

Table 1
Numerical value of exponent N in eq X (X=1 and 2) for Systems A (D_2O-saturated cement paste inserted in a reservoir of ethanol-h6), B (D_2O-saturated cement paste inserted in a reservoir of ethanol-h6 saturated with dye), and C (dye/ethanol-d6 saturated cement paste inserted in a reservoir of ethanol-d6) as determined by nonlinear least square fits of eq X (X=1 and 2) to the observed data in Fig. 7 (for F_c<0.6)

System	$N(X=1)$	$N(X=2)$
A	0.45 ± 0.02	0.35 ± 0.02
B	0.42 ± 0.02	0.36 ± 0.02
C	0.47 ± 0.02	

See text for further details.

3.5. Exchange rate of fluorescent dye

Unfortunately, it was impossible to obtain a resolved ^{1}H-NMR spectrum of a dye/ethanol solution confined within a cement paste. The residual, nondeuterated water peak of the ethanol completely masked the peaks originating from the dye. Moreover, a significant line broadening occurred due to a magnetic susceptibility difference between the confined fluid and the cement matrix, which completely masked any spectral details.

Thus, in order to determine the exchange rate of dye by NMR, the dye has to diffuse from the cement paste and into a surrounding liquid solution, in which the dye can be monitored by NMR.

Hence, a water (D_2O) saturated cement sample was immerged into a large reservoir of dye/ethanol-d6 solution (saturated with dye) for 3 days in order to exchange most of the water within the cement paste with the ethanol/dye solution. The pore volume of the cement sample was V_p=0.060 ml and the volume of the ethanol reservoir was V_E=0.318 ml. The resulting concentration of dye in ethanol-d6 (*within the cement paste*) is denoted C_1. This dye/ethanol containing cement paste was inserted into an ethanol-d6 solution and the exchange of dye monitored by ^{1}H-NMR.

Fig. 8 shows the ^{1}H-NMR spectra of fluorescent dye within the solution surrounding the cement paste during the exchange process. Fitting Eq. (5) to the data in Fig. 7B gives the diffusion coefficient of dye, D_{dye}, which becomes $(17.4+0.8)\times10^{-8}$ cm^2/s. This is more than 50% less than the diffusion of water and ethanol and originates from a larger molecular dimension of the dye compared to ethanol. The diffusion of dye from bulk ethanol into a water-saturated cement paste will probably be even slower due to the different solubility of dye in ethanol and water, respectively.

Table 2
Diffusion coefficients (D) for Systems A (D_2O-saturated cement paste inserted in a reservoir of ethanol-h6) and B (D_2O-saturated cement paste inserted in a reservoir of ethanol-h6 saturated with dye) as obtained by fitting Eq. (5) to the data in Fig. 7

System	$D(D_2O)$, cm^2/s	D(ethanol), cm^2/s
A	41 ± 4	72 ± 7
B	43 ± 3	58 ± 6

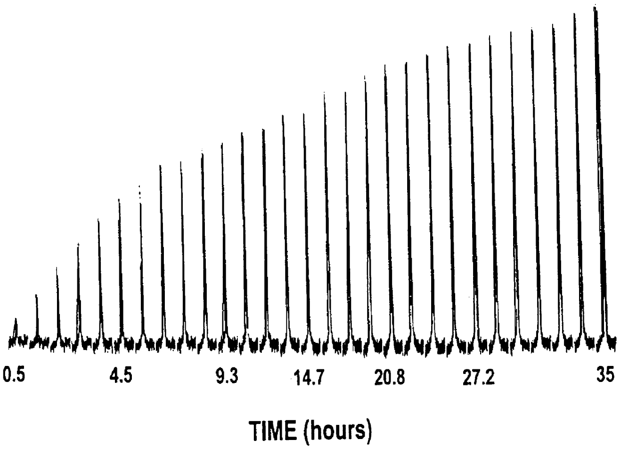

Fig. 8. ^{1}H-NMR spectra of fluorescent dye in ethanol-d6, surrounding the cement paste, as a function of time during diffusion of dye from the cement paste and into the surrounding ethanol-d6 solution.

From the observed signal intensity of fluorescent dye (in the surrounding ethanol-d6 solution; Fig. 7B,□), the concentration of dye at the end of the exchange process (5 days) can be calculated and amounts to C_2=(5.60+0.14)×10^{-4} g/g. If there is a partitioning (f) of dye between bulk ethanol-d6 and ethanol-d6 within the cement paste, we can write:

$$f = \frac{C_1}{C_0} = \frac{C_X}{C_2} \tag{6}$$

where C_X is the concentration of dye within the cement paste after the exchange process has reached equilibrium and C_0 is the maximum concentration of dye in bulk ethanol (=7.02×10^{-3} g/g). Mass conservation of the fluorescent dye within the complete system (cement paste–dye–ethanol-d6) gives Eq. (7):

$$C_1 V_p = C_X V_p + C_2 V_E. \tag{7}$$

Combining Eqs. (6) and (7) gives:

$$f = \frac{C_2}{C_0 + C_2} \frac{V_E}{V_p}. \tag{8}$$

Inserting numerical values of the parameters in Eq. (8) gives f=0.46+0.02, and shows that the concentration of dye in ethanol within a cement paste is approximately 50% less than the concentration of fluorescent dye in bulk ethanol, i.e., a partitioning takes place.

The ^{1}H-NMR spectra of the dye/ethanol solution before (Fig. 1) and after exchange (not shown) are identical and suggest that the fluorescent dye is inert, i.e., the fluorescent dye does not react with the cement paste. Moreover, no indication of any chemical reaction between the ethanol and the cement can be inferred from the spectral analysis.

4. Conclusion

^{1}H- and ^{2}H-NMR spectroscopy has been applied to monitor the exchange of water within a cement paste with ethanol/dye in a surrounding liquid solution.

A quantitative analysis of the NMR signal intensity of the exchanging fluids with processing time show that the exchange rate of water and ethanol are independent of the presence of dye. Provided that the volume of the surrounding solution—the reservoir—is large compared to the pore volume of the cement paste. Measuring the transport rate of dye in ethanol within a cement paste and into a surrounding ethanol solution suggest that the exchange rate of dye is smaller by a factor less than 0.5 compared to the exchange rate of water and ethanol.

Unfortunately, due to the small concentration of dissolved dye in ethanol combined with the magnetic susceptibility differences between confined fluid and cement matrix, it is not possible to obtain a resolved spectrum of the dye within the cement paste. To monitor the dye as a function of exchange time, only the liquid solution surrounding the cement paste can be subjected to NMR analysis. However, ^{1}H-NMR spectral analysis of a fluorescent dye/ethanol solution before and after exchange with a water-saturated cement paste suggest that both the dye and the ethanol are chemically inert, i.e., they do not react chemically with the cement paste.

Acknowledgments

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