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A simple semiempiric model for NMR relaxometry data of hydrating cement pastes

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Abstract

In this contribution, results from NMR relaxometry experiments on hydrating white cement pastes are presented. Nonexponential effects are discussed and quantified by stretched-exponential analysis. From the magnetization decay curves in transverse relaxation experiments, the degree of hydration is estimated and a semiempiric model is proposed describing the relationship between the microstructure development in the hydrating cement and the degree of hydration.

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1. Introduction

NMR relaxometry has been used for more than 20 years as a tool for following the hydration kinetics and microstructure development in hydrating cement pastes and related materials [1–8]. The most important merits of the technique are its noninvasive nature and the possibility to study real bulk samples with sizes of several millimeters or more in all three dimensions. Furthermore, the samples are accessible for mechanical or thermal manipulations during the experiment.

On the other hand, spin relaxation times as the main measured quantities are only indirectly related to the characteristics of the microstructure formed during hydration or to the chemical degree of hydration. Therefore, the interpretation of NMR relaxation data with respect to the material properties of the cement pastes under study is still problematic. In this paper, a simple semiempiric approach is suggested for establishing a relationship between the microstructure development and the chemical degree of hydration, which can also be estimated from the relaxometry data.

2. Materials and methods

NMR relaxometry was performed on a simple NMR relaxometer MRS 6 obtained from JSI, Ljubljana, Slovenia, operating at a proton resonance frequency of 22 MHz. Transverse relaxation times were measured using a simple spin echo sequence, longitudinal relaxation times were measured by means of an echo-detected saturation-recovery technique. This echo-detected approach was chosen in order to record only NMR signal contributions originating from the liquid phase. Details of the NMR relaxometry experiments and the mask-guided data evaluation procedures have been described in Refs. [9,10].

The cement used in the experiments was a commercial grade white cement Dyckerhoff weiβ CEM I 42.5 R obtained from Dyckerhoff, Wiesbaden. Samples were prepared by the manual mixing of cement and water quantities in a small plastic mixing container (for details, see Refs. [9,10]). White cement was used in order to minimize problems arising from increased spin relaxation due to paramagnetic iron content in the cement paste.

3. Results and discussion

3.1. Relaxation rates

Fig. 1 shows the typical development of the transverse and longitudinal relaxation rates in a hydrating white

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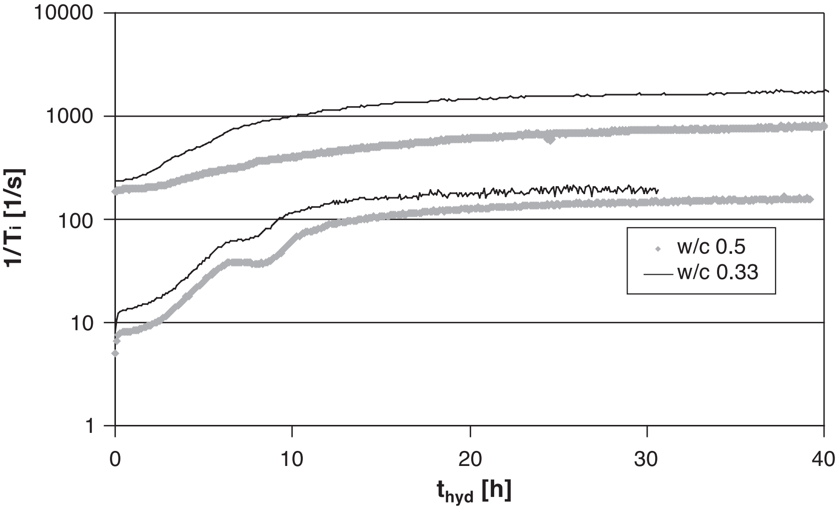

Fig. 1. Transverse (upper two curves) and longitudinal (lower two curves) relaxation rates measured on cement mixtures with different w/c ratios as a function of the hydration time.

cement paste for two different water/cement ratios (w/c). While the transverse relaxation rate qualitatively follows well the generally known hydration kinetics with a short induction period, a dormant period followed by the acceleration period and subsequent deceleration, the longitudinal relaxation rate exhibits a characteristic step structure, which is especially obvious in the sample with a w/c of 0.5. A systematic study on this structure was recently reported [10]. On the basis of these results and the qualitative behaviour of the transverse relaxation data, we consider the transverse relaxation rate to be a more straightforward indicator for the microstructure formation than the longitudinal relaxation rate. Furthermore, the spin echo data can also be used for estimating the amount of liquid water remaining in the paste: This information is contained in the spin magnetization extrapolated to zero echo time. This quantity is available as the amplitude of the echo decay curve fitted to the data in determining the relaxation rate.

3.2. Nonexponentiality and degree of hydration

However, analyzing the experimental echo decay curves is complicated by the nonexponential behaviour of these data. A quantitative representation of the degree of nonexponentiality of the relaxation processes can be obtained by fitting a stretched-exponential curve to the experimental data (see Fig. 2).

$$M(t) = A\exp[-(t/\tilde{T})^{\beta}] \qquad (1)$$

The more β deviates from 1, the more nonexponential the magnetization decay is. Exponents below 1 correspond to the multiexponential relaxation behaviour (i.e., to micro-

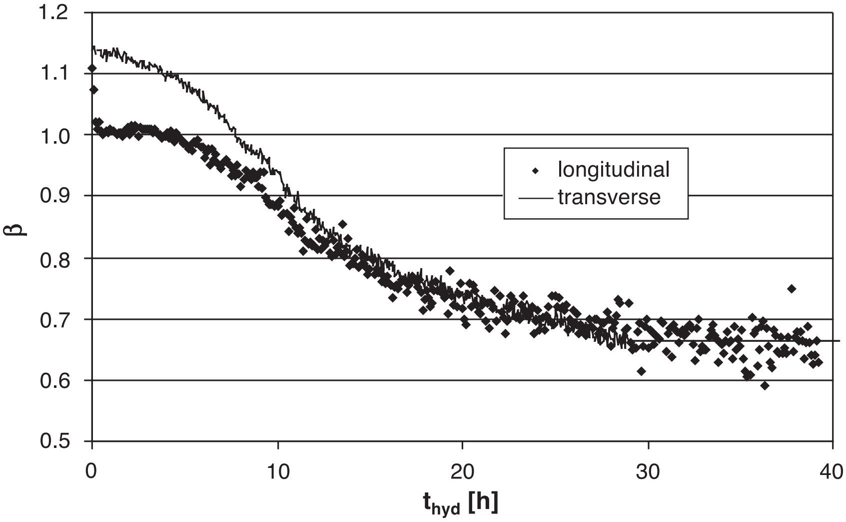

Fig. 2. Exponent β obtained in stretched-exponential evaluations of relaxometry data obtained on a w/c = 0.5 white cement sample. The initial behaviour for the transverse relaxation is influenced by the diffusive signal attenuation in internal magnetic field gradients.

scopically inhomogeneous environments with incomplete exchange on the time scale of the relaxation), exponents above 1 in the transverse relaxation curves can be explained by a superposition of relaxation and diffusion effects in internal magnetic field gradients [9]. Notable internal gradients in white cement pastes have been observed also in PFG NMR experiments [8] so that the initial values for β are consistent with other observations. In longitudinal relaxation, diffusive echo attenuation can be ruled out as an explanation for β values above 1. Nevertheless, we also find such exponents in the evaluation curves for the first longitudinal relaxation measurements. They can be explained by a fast increase in the longitudinal relaxation rate during the induction period. This interpretation could be confirmed by fitting the initial magnetization decay curves with an explicitly hydration-time-dependent relaxation rate. At later hydration times, the β values resulting from stretched exponential analysis of both the transverse and the longitudinal relaxation times reach very similar values as diffusion-related effects become less relevant due to shorter time scales and decrease in the water self-diffusion coefficient [8], which in turn reduces the diffusion artifacts in the spin-echo decay curves.

While the stretched exponential model is very effective in quantifying the nonexponentiality of a magnetization decay curve, it is not appropriate for evaluating the signal amplitudes at zero echo time as the derivative of the function exhibits there an infinity point for $\beta < 1$. This was pointed out in Ref. [11]. In that paper, a modified evaluation function was suggested in which this problem is eliminated. However, this function proved to be unsuitable for the automatic evaluation of the series of magnetization decay curves in this work, as it tends to be numerically unstable for near-exponential curves. For the evaluation of the signal amplitudes, we therefore resorted to using single exponential evaluations over a short time window. In this case, an average relaxation rate and a good value for the initial signal amplitude are obtained from the fit. The appropriateness of the mask-defined short time windows was checked by examination of selected evaluation curves and on the basis of the correlation coefficients.

From the signal amplitudes in this evaluation, the chemical degree of hydration $h(t_{\mathrm{hyd}})$ of the cement paste can be determined as:

$$h(t_{\mathrm{hyd}}) = \frac{w}{w_o}\left(1 - \frac{A(t_{\mathrm{hyd}})}{A_{\mathrm{initial}}}\right) \tag{2}$$

with w denoting the w/c of the paste, w_o the stoichiometrical w/c needed for full hydration, $A(t_{\mathrm{hyd}})$ the signal amplitude of the magnetization decay curve under consideration and A_{initial} the amplitude in the first magnetization decay curve obtained on the fresh sample.

In Fig. 3, the time dependence of the degree of hydration obtained for a cement paste with a w/c of 0.5 is given (assuming a stoichiometrical w/c of 0.25). In addition to the experimentally determined values, fitted curves are included on the basis of a recently suggested model for the hydration kinetics of cement [12] and also by means of the function

$$h(t) = A\frac{1 - a_1 e^{-t/T_{h1}} - a_2 e^{-t/T_{h2}}}{1 + e^{-\frac{t-t_d}{T_{h3}}}} + h_o \tag{3}$$

where A, a_1, a_2, t_d, T_{h1}, T_{h2}, T_{h3} and h_o are fitting parameters (in practice, a_2 was set to be $1 - a_1$ and A as $1 - h_o$ in order to reduce the number of fitting parameters).

This latter function was empirically chosen to fit the experimental course of the degree of hydration during the first few days of hydration very well and thus provide a smoothened data set for further analysis of the data. As it essentially consists of a Fermi function modulated by a biexponential decay, it will be referred to as FerBiex model in the rest of the paper. In contrast to the model by Tschichholz and Zanni [12], the fitting function in the FerBiex model is an explicit function of the hydration time

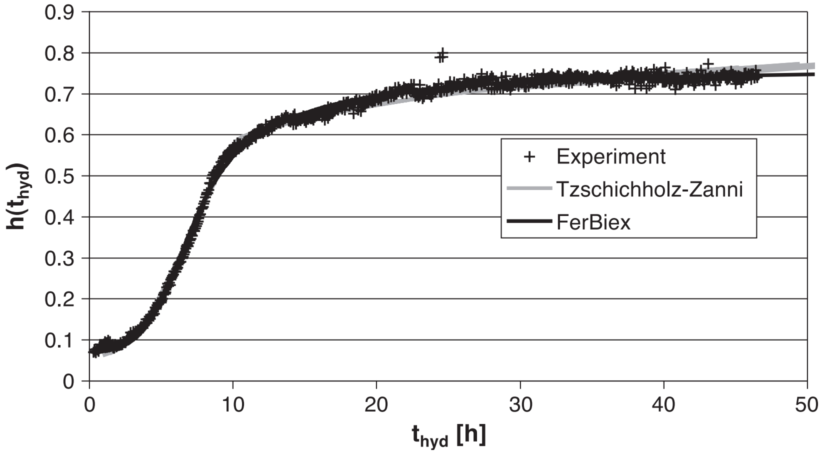

Fig. 3. Experimental data on the degree of hydration determined from the exponential analysis of the spin echo data for a white cement paste of w/c = 0.5. The initial data points corresponding to the induction period have been omitted in the graph and incorporated as a constant offset h_o in the fitting of the two models to the experimental data.

and thus much better fitted in order to give a smooth representation of the degree of hydration for further evaluations. The first few data points corresponding to the induction period have been neglected for the evaluation in both cases and were integrated into a constant offset value for the fitted data.

3.3. Relationship between degree of hydration and microstructure development

In Fig. 4, the transverse relaxation rates observed on the same sample are plotted as a function of the degree of hydration—once using the experimentally determined values for the degree of hydration and once using the values resulting from fitting a the FerBiex model to the degree of hydration data. As can be seen from the graph, the use of the FerBiex fitting results instead of the unsmoothened experimental data reduces the noise level in the plot considerably. Further evaluations of the relationship between relaxation rate and degree of hydration therefore were carried out using the FerBiex data.

The transverse relaxation rate is related to the pore structure. The most simple assumption on this relationship is a two-phase fast exchange model (see, e.g., Ref. [13]). In this case, the transverse relaxation rate depends linearly on the surface/volume ratio (S/V):

$$\frac{1}{T_2} = \frac{1}{T_{2\mathrm{bulk}}} + a\frac{\mathrm{S}}{\mathrm{V}} \tag{4}$$

where $T_{2\mathrm{bulk}}$ denotes the relaxation time of the bulk liquid and a is the surface relaxivity of the pore wall material. While the pore sizes in a cement matrix are small enough to provide appropriate conditions for two-phase fast exchange, it should be noted that

- ○ A distribution of pores with various S/V values leads to a corresponding distribution of relaxation times if no fast exchange between all pore sizes is provided.
- ○ In very small pores, the surface relaxivity was experimentally found to decrease due to diffusion along the curvature of the pore surface. This has been studied with great care in the case of longitudinal relaxation (e.g., Ref. [14]). For transverse relaxation, there are no similarly systematic studies yet. This implies that using the two-phase fast exchange model might underestimate the true S/V in the cement. However, due to the shorter time scale of transverse relaxation compared to longitudinal relaxation, we can expect the decrease in the surface relaxivity due to geometry to be smaller than in the longitudinal case. This fact might even be mirrored in the relaxation data in Fig. 1: while the transverse relaxation times increase monotonically throughout the observation time, the liquid phase longitudinal relaxation seems to reach a plateau value after about 20 h of hydration.
- ○ The surface relaxivity is a property of the individual materials making up the pore walls. If changes in the pore wall chemistry would lead to considerable changes in the relaxivity, this could again result in wrong S/V estimates on the basis of the two-phase fast exchange model.

Despite all the problems associated with the two-phase fast exchange model, the experimentally observed values of transverse relaxation still seem to provide a valid indication of the pore structure development when interpreted along the lines of this model. Therefore, in the rest of the paper, it will be used to determine the change of the S/V from the data.

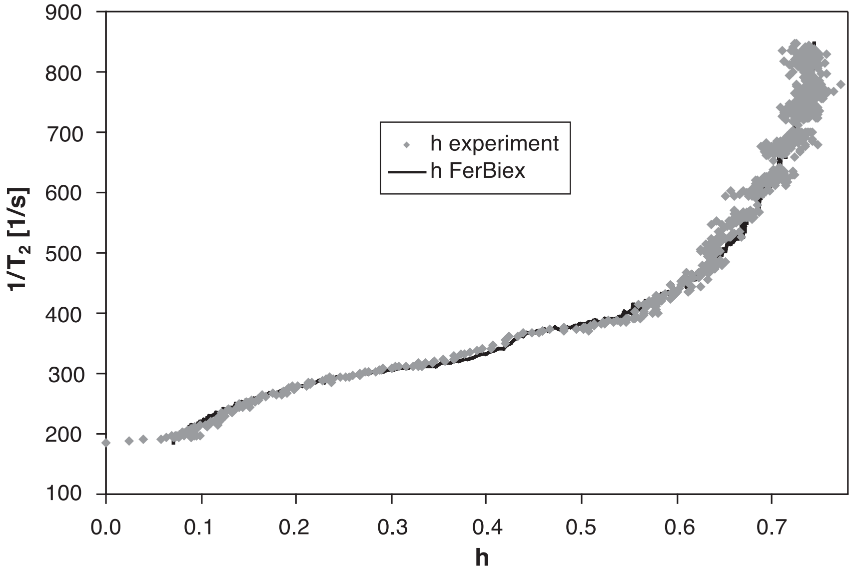

Fig. 4. Transverse relaxation rate in a hydrating cement paste with w/c = 0.5 as a function of the degree of hydration. The relaxation rates have been plotted once as a function of the unsmoothened experimental degree of hydration data and once as a function of the fitted results using the FerBiex model.

Doing so, the data in Fig. 4 represent an experimental relationship between the microstructure formation and the course of the chemical reaction during the hydration of the cement. The challenge now is to find an appropriate model to describe the relationship between both quantities.

An obvious oversimplification but a starting point for the development of more refined models is the assumption of the water in the cement paste being confined to a constant number of shrinking pores. The S/V as function of the chemical degree of hydration for such a system is:

$$
\begin{aligned}
O(h) &= \frac{4\pi(r(h))^2}{4/3\pi(r(h))^3} \\
&= \frac{4\pi\left(\sqrt[3]{\frac{3}{4\pi}V_o\frac{x_o-\varepsilon h}{x_o}}\right)^2}{4/3\pi\left(\sqrt[3]{\frac{3}{4\pi}V_o\left(\frac{x_o-\varepsilon h}{x_o}\right)}\right)^3} \\
&= 3\sqrt[3]{\frac{4\pi}{3V_o}}\frac{1}{\sqrt[3]{\frac{x_o-\varepsilon h}{x_o}}}
\end{aligned}
\qquad (5)
$$

With V_o denoting the originally available pore volume in the paste, x_o the water content as a multiple of the stoichiometrical water demand of the cement and ε the change in the volume of the hydration phases formed compared to the original cement clinker and water. While this latter quantity is well known for the main hydration phases formed at late hydration stages (see, e.g., Ref. [15]), this is not the case for the originally formed hydration phases where phases resulting in volume increase (such as ettringite) and phases associated with a decrease in the volume (such as tobermorite/portlandite) are formed at the same time. As the present analysis is concerned mainly with the first days of hydration, we will for the sake of simplicity set the factor ε as 1 for the further discussions in this paper.

In reality, Eq. (5) is of course an unrealistic picture, as the water during cement hydration is confined into a system of pores that tend to be separated into smaller pores during the hydration by the formation of an increasingly thick network of lamellar and acicular hydrate phase crystallites. A very rough possibility to include this into the shrinking pore model is to assume that the number of pores in the hydrating cement stone matrix increases with the course of the hydration progress. This can be incorporated into the model by means of a pore number multiplication function (PNMF) $n(h)$:

$$
O(h) = 3\sqrt[3]{\frac{4\pi}{3V_o}}\frac{(n(h))^{1/3}}{\sqrt[3]{\left(\frac{x_o-\varepsilon h}{x_o}\right)}} \qquad (6)
$$

In order to turn this pore number multiplication model (PNMM) into a viable description of the microstructure development in a hydrating cement paste, an appropriate functional form for the PNMF is needed.

Considering the experimentally observed development of the relaxation times and the well-known fact that there is a depercolation process taking place at later hydration stages in the cement, we need a PNMF that exhibits a near-linear behaviour in the initial stages of the hydration followed by a strong increase at higher degrees of hydration.

A simple function that complies with these requirements is

$$
n(h) = N_o(1 + ah^c\left(1 + g\exp\left(\frac{h-h_o}{b}\right)\right) \qquad (7)
$$

where N_o stands for the initial number of droplets per volume unit and a, c, g, b and h_o are fitting parameters.

However, tentative use of this function within the framework of the PNMM leads to several problems:

○ The derivative of the function in Eq. (7) increases monotonically with the degree of hydration, i.e., the PNMF is steepest when reaching full hydration. This is physically not very plausible.

○ When fitting this PNMF to experimental data, the numerical uncertainties for a, h_o and g were found to remain very big and often even to diverge when using the model with Origin 6.0's nonlinear curve fitting capabilities.

The failures of the simple PNMF in Eq. (7) lead to the search for a better PNMF that avoids those shortcomings.

$$
n(h) = N_o\left(1 + ah^c\left(1 + \frac{g}{1+\exp\left(-\frac{h-h_o}{b}\right)}\right)\right)^d \qquad (8)
$$

with d, denoting an additional parameter was found to provide a PNMF that overcomes the problems posed by the PNMF in Eq. (7): The use of the Fermi function instead of the simple exponential function reduces the increase in the droplet multiplication at higher degrees of hydration. The parameter d was not used as a free fitting parameter. However, it was found that using a value of $d=2$ increases the numerical stability when fitting the model to experimental data. Other values such as 1 and 3 were tested for d too. While no better overall correspondence with the experimental data could be obtained, the numerical stability was found to be much poorer in this case.

The parameter c was used as a free parameter in some experiments. However, it was typically found to take on values close 2/3 in fitting experiments with the PNMF in Eq. (8). Therefore, at the later fitting runs, it was set to this value in order to reduce the number of free-fitting parameters in the model.

In Fig. 5, the model with the PNMF of Eq. (8) is fitted to the experimental data (using the hydration degrees resulting

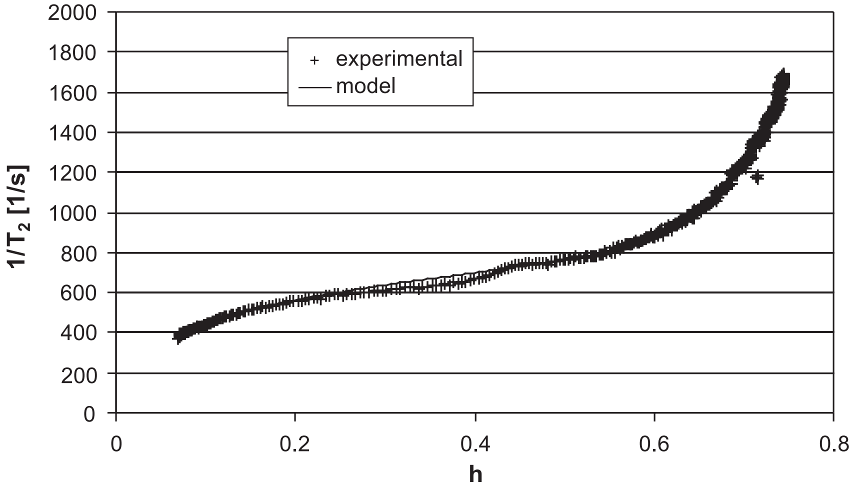

Fig. 5. Experimentally determined relaxation rates and fitted values according to the PNMM as a function of the degree of hydration for a white cement sample with w/c = 0.5 (data from Fig. 4).

from the data analysis according to the FerBiex model). In Fig. 6, the same data are plotted as a function of the hydration time. As we can see from the figures, there is a good correspondence between the model and the experimental data throughout the whole observation period. At later hydration times, the scatter in the data calculated from the experimentally determined degrees of hydration becomes quite high due to the increasingly poor signal/noise ratio and the short time windows for the determination of h. Furthermore, the PNMF is steepest close to h_o. The correlation between the fitted curve and the experimental data in Fig. 5 is better than .995. A similarly good correlation to the experimental results is also reached for the analysis of the hydration data for the sample with a w/c of 0.33.

The observation of cement hydration with NMR relaxometry becomes more and more difficult at later hydration stages as the liquid signal intensity available decreases and the shorter relaxation times further limit the experimental possibilities. These two factors especially complicate the determination of the degree of hydration from experimental data. Therefore, we can presently not validate the model for higher degrees of hydration on the basis of actual experimental data. However, what we can do is to extrapolate the model to higher degrees of hydration and compare the extrapolated values to data from other experiments reported on structure formation in hydrating cement pastes. The quantity typically determined in such studies is the pore surface in the cement paste. As the absolute values for the inner surface in hydrating cement pastes are still an open

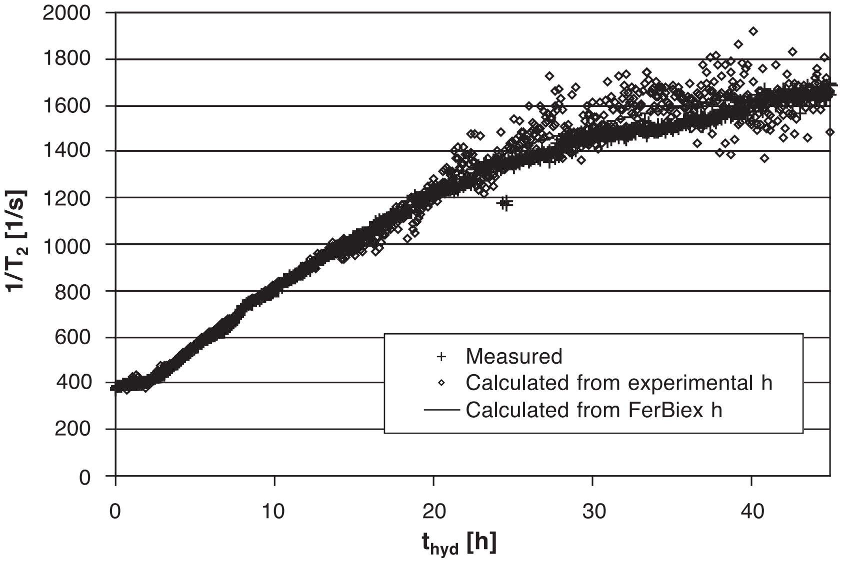

Fig. 6. Relaxation rates calculated from the PNMM as a function of the hydration time, same sample as in Figs. 4 and 5. The high scatter in the values calculated directly from the experimental degree of hydration data is due to the increasingly poor signal/noise ratio in the experimentally determined degree of hydration and due to the high slope of the PNMF around h_o.

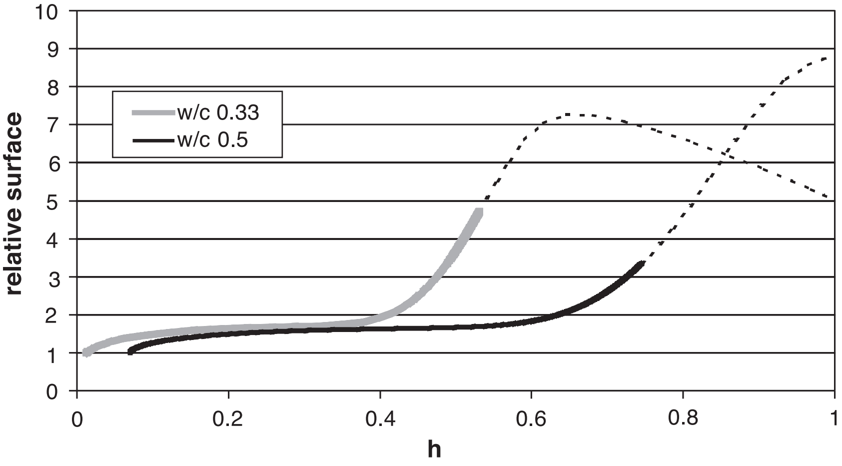

Fig. 7. Relative inner surface as a function of the degree of hydration for two hydrating white cement samples with different w/c calculated on the basis of the PNMM. The dashed lines correspond to the extrapolation in the range of data not covered by experimental data.

question, we opted not to try an absolute calibration of the surface values but to stick with the relative changes such as recommended in Ref. [16]. The relative change in the pore surface can be easily computed from the PNMF.

The corresponding data are plotted in Fig. 7 as a function of the degree of hydration and in Fig. 8 as a function of the hydration time (using the extrapolated hydration kinetics according to the FerBiex model). As the PNMM was derived on the basis of a multiplication in the number of droplets or pores in the cement stone matrix, it is of interest to consider the multiplication factor in the pore number too: it was found to be several thousands for all relaxation time series evaluated up to now.

The extrapolated values and the stronger increase in the relative pore surface for higher w/c ratios are in quite good agreement with results both from NMR data by other groups and from other techniques as reported in Ref. [17]. The relatively small increase in the pore surface in both our experiments and the other work mentioned here is due to the fact that there is a tremendous increase in the pore surface already during the first few minutes of hydration, i.e., during the first parts of the induction period. This part of cement hydration is still not experimentally accessible in a satisfying way, as it is quite fast and would need to be measured during the mixing of the paste. Obviously, high amounts of pore surface are already formed during this period. This problem is not unique to NMR relaxometry but exists with all experimental techniques available for nondestructive determination of the S/V in hydrating cement pastes. The decrease of the extrapolated S/V in the sample with a w/c of 0.33 for longer hydration times may seem very surprising at a first glance. However, there are several studies in the literature in which a maximum in the S/V is reported for samples with a lower w/c (e.g., Refs. [17,18]). A possible explanation is the limitation of further surface growth by the reduced amount of water-filled pore volume available.

To conclude, we have presented a simple model to establish a relationship between microstructure formation in hydrating cement pastes as seen by NMR relaxation rates and the chemical degree of hydration in the pastes. As a basis for developing the model, we used the fact that transverse relaxometry NMR data not only allow the determination of relaxation rates but also of the chemical degree of hydration—a fact that has scarcely been drawn use of in

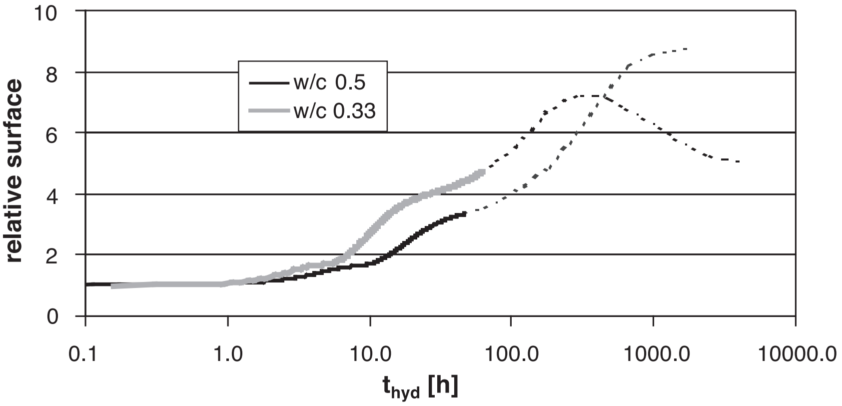

Fig. 8. Development of the inner surface as a function of the hydration time in the pastes shown in Fig. 7. For the extrapolation time course of the degree of hydration, the fit data according to the FerBiex model were used. Again, the dashed lines represent the range of data not covered by experimental data.

earlier work on cement hydration. Despite some very crude assumptions, the model allows both a good fit of the actual experimental data obtained during the first 2 days of hydration in cement pastes and decent extrapolations to higher degrees of hydration.

Further steps in developing and validating the model by extending the evaluations to other cement paste formulations containing additives and to data on the diffusion in hydrating cement are under way. Another interesting question would be to compare the PNMM with the relationship between the degree of hydration and pore structure resulting from simulation models such as the NIST model [19]. Such comparisons could also provide a basis for developing other functional forms for the PNMF. The availability of a simple model providing an analytical expression for the relationship between the degree of hydration and the microstructure development offers a convenient tool for bridging the gap between experimental information and simulations.

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