Nuclear Spin Relaxation and Water Self-diffusion in Hardening Magnesium Oxychloride Cement

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In this contribution, we report the results of NMR studies of the behaviour of water in a hydrating Sorel cement paste with a composition close to the stoichiometric optimum. Both the transverse spin-relaxation behaviour and water self-diffusion were studied in two separate experiments performed on samples on the basis of the same formulation. While there is a very strong initial decrease in the transverse relaxation time of the water in the paste, the diffusion coefficient is found to decrease mainly at later times of the hydration process where the decrease of the transverse relaxation time has already strongly slowed down. After about 6 h of the hardening process, the signal intensity available for a pulsed gradient diffusometry experiment is not sufficient any more for reliable measurements of the diffusion coefficients.

Key words: Oxychloride Cement; Diffusion; Magnetic Resonance.

Magnesium oxychloride cements (first described by Sorel [1]) are primarily used as a jointless flooring material. They are also used in certain plaster and stucco applications and as binder for the production of light-weight construction plates from coarse wood chips. Mg oxychloride cement is also discussed as a possible material for preventing mining damages from old salt mines and for sealing hazardous waste dumps in such old mines [2]. Compared to other binder systems, such as portland cement and gypsum, magnesium oxychloride cement provides a higher mechanical strength [3].

Oxychloride cements are typically prepared from MgO powder and a highly concentrated solution of $MgCl_2$. In contrast to classical cement materials, the pH values for such pastes are typically in the acidic range. For practical application of oxychloride cements one is usually interested in a composition close to a molar ratio of (5:1:13) of ($MgO : MgCl_2$: water) [4]. Oxychloride hydrate phases of this composition are also important in the formation of early strength of the hardening mixtures.

Water transport processes play a crucial role in the hardening of the oxychloride cements, and also in the later carbonatization and corrosion processes. NMR relaxometry and diffusometry offer a destruction-free approach for studying the dynamics of the fluid pore water in hydrating construction materials such as ordinary cements [5, 6], slag cements [7, 8] and gypsum [9]. Here, we report the application of these techniques to magnesium oxychloride cements.

Materials and Methods

Magnesium oxychloride cement samples were prepared from food grade "heavy" magnesium oxide powder obtained from Merck, Darmstadt, and from a 5 M watery solution of magnesium chloride hexahydrate (analytical grade, also from Merck, Darmstadt). Pastes were mixed from 5 g MgO and 5 ml of the $MgCl_2$ solution by means of mechanical stirring with a plastics (PVC) rod in small rectangular polypropylene containers. For the experiments, the samples were filled either in plastics sample tubes produced from disposable 3 ml polypropylene syringes with a Luer-Lock connector (Becton-Dickinson, Meylan, France) for the relaxometry studies or in small segments of 5 mm diameter glass tubes of about 1.5 cm

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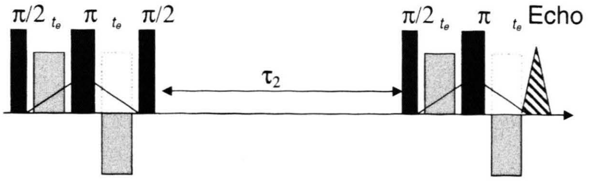

Fig. 1. 5-Pulse sequence for PFG diffusometry on a sample with strong internal magentic field gradients. While the 180° pulses reset the phase memory due to the movement of the spins in the internal magnetic field gradient during the time between the first 90° pulses, the influence of the alternating gradient pulses is not reset and thus contributes to the diffusive signal attenuation over the whole observation time.

length, which then were put into 7 mm diameter test tubes for the PFG NMR experiments.

NMR relaxometry was performed using a simple spin-echo-sequence (90 - t_e - 180 - t_e - Echo) on an MRS 6 spectrometer (Jozef-Stefan institute, Ljubljana, Slovenia) with a 0.5 T permanent magnet system and a proton NMR frequency of 22 MHz. PFG NMR was performed by means of the home-built Fegris 400 NT diffusometry facility [10], operating at a magnetic field strenght of 9.4 T and offering the possibility to use gradient pulses with strenghts of up to about 30 T/m. The pulse sequence used in the experiments is depicted in Figure 1. This pulse sequence [11] offers the possibility to perform PFG diffusometry experiments in the presence of inner magnetic field gradients in a heterogeneous sample. The echo attenuation $\Psi(G)$ as a function of the gradient pulse amplitude G is given as

$$\Psi(G) = \frac{S(G)}{S(0)} = \exp\left(-\gamma^2\delta^2G^2(4\tau_2 + 6t_e - \frac{2}{3}\delta)D\right)$$

$$= \exp(-F(G)D)$$

with δ denoting the duration of the gradient pulses and under the assumption that the gradient pulses are centered in the interval between the 90° pulse and the 180° pulse.

Comparative experiments with an ordinary PFG stimulated echo sequence with this 5-pulse sequence showed that there are considerable magnetic field gradients in oxychloride cement pastes despite the absence of notable paramagnetic constituents. These gradients are mainly due to the differences in the diamagnetic susceptibility of the $MgCl_2$ solution and to the MgO particles which are only on the order of several ppm but nevertheless can lead to quite strong internal gradients on the order of 0.1 T/m or more due to the small grain size and the high static magnetic field. All diffusion data presented in this article were obtained using the 5-pulse sequence in order to compensate the effect of the internal gradients.

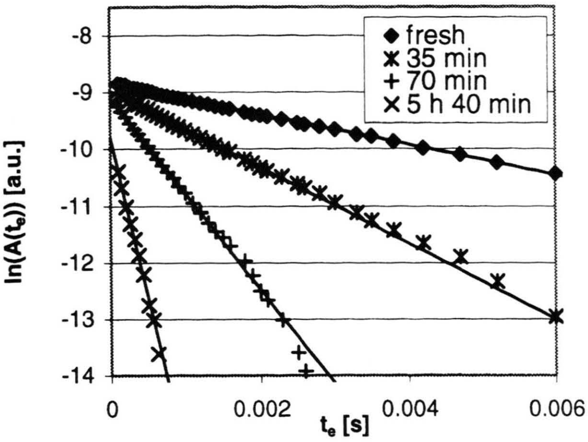

Fig. 2. Spin echo decay curves for a hydrating sorel cement mixture at different times after preparation. The lines represent fit curves from linear regression. Correlation for all regression curves is better than 0.99. The range of the data used in fitting was determined in a way that noise signals and digitization effects were not included.

Results and Discussion

In Fig. 2, examples of echo attenuation curves obtained at different times in a series of spin-echo experiments on a hydrating sorel cement sample are given. We see that the relaxation time decreases very strongly with the hardening time. In all curves, only small systematic deviations from a single exponential decay $A(2t_e) = A(0)\exp(-2t_e/T_2)$ can be observed (only for the curve after 35 min, a slightly polyexponential behaviour could be discerned). Furthermore, we can see that the overall amplitude $A(0)$ of the echo signal also decreases with the hardening time. This decrease can be attributed to the binding of water into solid oxychloride hydrate phases where it is sufficiently immobile not to contribute to a spin echo signal under the experimental conditions used.

In Fig. 3, examples for echo attenuation curves obtained in a series of PFG experiments on a sample prepared in the same way are given as functions of the echo attenuation factor $F(G)$ corresponding to the gradient pulses.

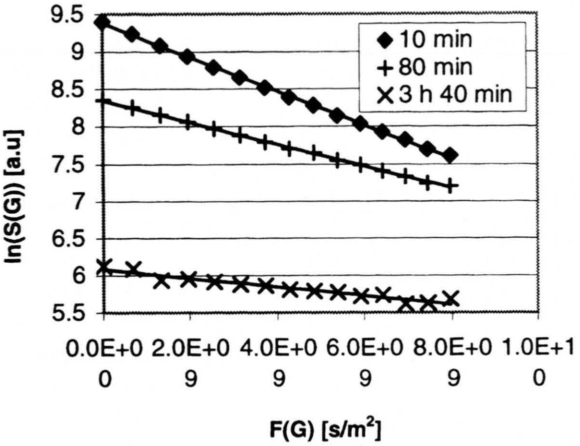

Fig. 3. Echo attenuation curves from PFG NMR experiments on a hardening oxychloride cement paste at three different hardening times (abscissa: 0 - 10^{10}). Within the experimental accuracy, all echo decay curves are monoexponential. Diffusion coefficients were evaluated by linear regression over all data points.

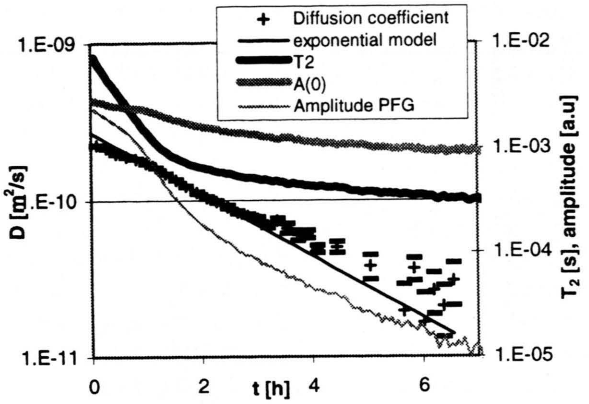

Fig. 4. Water self-diffusion coefficient, transverse relaxation time and signal amplitude as a function of the hardening time in an Mg oxychloride cement paste. The fit of an exponential model to the diffusion coefficient decrease shows that the initial decrease is less pronounced than the one observed when the transverse relaxation time is already decreasing more slowly. The big scattering of the diffusion data at long hardening times is mainly due to the very poor signal available for the PFG experiment at these times.

Within the range of experimental accuracy, also these echo attenuation curves can be considered to be monoexponential. This suggests that the obtained diffusion coefficients are not just mean values for a very broad distribution of diffusion coefficients but are quite representative for the diffusion behaviour of most of the fluid in the pores of the hardening cement paste.

In Fig. 4, the transverse relaxation time, the self-diffusion coefficient and the echo signal amplitude $A(0)$ are given as functions of the hardening time of the oxychloride paste. Furthermore, also the available signal amplitude for the echo in the PFG experiment is given (i. e. the product $A(0)\exp(-4t_e/T_2)$. The very strong decrease of this signal amplitude is the reason for problems in measuring diffusion coefficients in the paste at later hardening times, which is obvious from the big error bars. Along with the diffusion data, a phenomenological fit of an exponential model $D(t) = D(0)\exp(-at)$ is given. The initial data up to about 1 h of hydration were not used in this fit. As one can see from the figure, the diffusion coefficient decrease during this phase is slower than the phenomenological fit.

When comparing the hardening time dependence of the different quantities in Fig. 4, the most striking feature is the strong decrease of the transverse relaxation time at early hardening phases. While also the diffusion coefficient and the echo amplitude show a decrease in this phase of the hardening process, the decrease in these two parameters becomes steeper only after the decrease in the relaxation time has already started to level off. This suggests a three-phase mechanism in the hardening process:

- Rapid formation of a gel-like phase, which has already substantially proceeded even before the first echo measurement, as can be seen from the fact that even in the first experiment a diffusion coefficient is recorded that is by about a factor of 10 below the value for free water; diffusion measurements in pastes of other mineral binder materials, such as cement [6] or slag cements [8], show much less reduced initial water self-diffusion coefficients compared to free water.
- Ripening of the gel-phase, during which there is only minor binding of water and during which the diffusion coefficient is also undergoing only minor changes.
- Increased binding of water into the solid phase and formation of massive oxychloride-hydrate crystals that lead to an increase in the tortuosity of the pore system on a sub-μm length scale and thus to a reduction of the water-self-diffusion coefficient.

As we can see from the loss in the echo signal amplitude, the originally available water in a paste with a composition close to the stoichiometric optimum of (5:1:13) is almost completely used up during this process. The time-scale on which this water immobilization occurs compares quite well with earlier X-ray scattering and electron microscopy observations [12, 13] in which a rapid formation of oxychloride phases was observed after 1 to 2 hours while in the earlier hydration stages much of the Mg was not observable in crystalline form and is thus supposed to be contained in a gel-phase.

A direct correlation of the initial fast decrease of the relaxation time with the observations in mineralogical studies of oxychloride cement hardening cannot be made, as both the time resolution of these experiments was not high enough and also gel-like-phases are typically not accessible to large-angle scattering methods, which was the main method in the mineralogical studies of oxychloride cement hardening up to now.

Conclusion

Oxychloride cement hydration can be studied by NMR relaxometry and NMR diffusometry. While the observed behaviour of the echo signal amplitude and the measured water self-diffusion coefficient follow quite similiar time-dependences, the transverse relaxation time shows an initial very pronounced decrease, which is not observable in the amplitude and diffusion data. This shows that the relationship between the relaxation time and the actual course of the hardening process is somewhat looser than the relationship between the diffusion coefficient and the hydration process. The relatively fast hardening process and the easy availability of high-purity constituents make Mg oxychloride cements a good model system to study some general aspects of hardening mineral binder systems, which might be more difficult to analyze in other materials such as ordinary Portland cement. Furthermore, NMR relaxometry might be a good candidate for studying the reaction speed of Sorel cements prepared from different types of MgO, which was suggested as an important part of quality control efforts in [4].

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