NACL INTERACTION DURING HYDRATION AS STUDIED BY NMR

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Abstract

With freshwater getting scares seawater, i.e., water containing NaCl, can become the only viable option for making concrete. Although a lot of research had been directed to understanding the role of water in cement hydration, not much is known about the interaction of the Na^+ and Cl^- with cement paste during drying. A problem is that available techniques like, i.e., XRD, SEM, and EDX, for measuring the microstructure and the methods for determining the concentration of Na+, Cl- ions in pore solutions are either indirect or invasive and moreover often destructive, which consequently may lead to inadequate interpretations. Using a specially designed Nuclear Magnetic Resonance (NMR) setup, the ^1H, ^{23}Na and ^{35}Cl content in cementitious materials can be measured quasi-simultaneously and hence give us direct information on the interaction of the ions and the microstructure development. We have studied the influence factor, i.e., the water-cement ratio, on the microstructure development and the binding of Cl^- and Na^+. It was found that during the initial hydration stage more Cl^- is bound in comparison to Na^+ . This is reversed during the acceleration period after which there is a preference for binding of Na^+ in comparison to Cl^-. Increase of W/C ratio results in less binding capability of Na^+ and Cl^-.

Keywords: Cement-based materials; NMR; Hydration process; Sodium chloride

1. INTRODUCTION

When considering Alkali-Silica Reaction (ASR) or chloride attack, there are strict limits on the concentration of both Na^+ and Cl^- ions, in reinforced concrete, pre-stressed concrete and plain concrete [1-3]. However, it can still be that in special cases sodium chloride (NaCl) is introduced in the preparation of concrete. One can think of job sites where there is a lack of natural fresh water, e.g. islands, seacoasts and places near saline lakes, and hence in these cases often water containing NaCl is the most viable option for producing concrete. Therefore a better understanding of the microstructure development during cement hydration process with NaCl solutions may lead to an improved design for cement-based materials.

However, available techniques like i.e., XRD, SEM, and EDX, for measuring the microstructure and the methods for determining the concentration of Na^+, Cl^- ions in pore solutions, e.g., pore solution compression method, are either indirect or invasive and moreover often destructive, which consequently may lead to inadequate interpretations. Hence the influence of these ions on hydration is not only poorly understood, but there has also a lack of non-destructive techniques to systematically study the interaction of ions during hydration. Using Nuclear Magnetic Resonance (NMR) one can probe the microstructure in cement-based materials, and various studies [4-8] have focused on microstructure evolution and water consumption in cement paste during hydration. Despite the lower sensitivity of NMR for ^{23}Na and ^{35}Cl NMR can be used to study the ion transport/interaction in cement [9,10].

We will first present the specialized NMR as used in this study, which allows us to quasi-simultaneously measure the ^{1}H, ^{23}Na and ^{35}Cl. Next, we will discuss the measurements of the hydration with NaCl solutions followed by discussion and conclusions.

2. NMR SETUP

Nuclear Magnetic Resonance (NMR) is a non-destructive technique for quantitatively mapping certain elements. During an NMR experiment, the magnetic moments of the nuclei are manipulated by suitably chosen Radio Frequency (RF) fields. The resonance condition for the nuclei is given by:

$$f = \gamma B \tag{1}$$

Where f is the frequency of the alternating field, γ is the gyromagnetic ratio of the nuclei, and B is the magnitude of the externally applied static magnetic field. Hence according to the resonance condition, the measurement can be made only sensitive to ^{1}H, ^{23}Na or ^{35}Cl.

In an NMR experiment the magnetic moments of hydrogen nuclei are manipulated by suitably chosen alternating RF pulses, leading to a so-called Hahn spin-echo signal. The spin-echo signal will give information about the rate at which this magnetic excitation of the spins decays. The system will return to its equilibrium by two mechanisms: interactions between the nuclei themselves, causing the so-called spin-spin relaxation, and interactions between the nuclei and their environment, causing the so-called spin-lattice relaxation. Assuming that both mechanisms give rise to a single exponential relaxation and that spin lattice relaxation is much slower than the spin-spin relaxation, the magnitude of the NMR spin-echo signal is given (see, e.g., [11]):

$$S \sim G\rho\left[1 - \exp\left(-\frac{TR}{T_1}\right)\right]\exp\left(-\frac{TE}{T_2}\right) \tag{2}$$

where G is the relative sensitivity (G=1 for ^{1}H, 0.0925 for ^{23}Na and 0.0035 for ^{35}Cl), ρ the density, T_1 is the spin-lattice relaxation time, TR is the repetition time of the spin echo experiment, T_2 is the spin-spin or transverse relaxation time and TE is the so-called spin-echo time. In general, the repetition time is chosen as TR ~ $4T_1$ and hence the signal will only depend on the T_2 relaxation and short-spin echo times are preferred.

As the nuclei are moving randomly because of Brownian motion during an NMR experiment, they are also probing the pore-space. By Brownstein and Tarr [12] it was shown that both the T_1 and T_2 relaxation of water in the pores of a material can be related to the pore size:

$$\frac{1}{T_{1,2}} = \frac{1}{T_{bulk}} + \rho_{1,2}\frac{S}{V} \tag{3}$$

Where $\rho_{1,2}$ is the so-called surface relaxivity for the T_1 and T_2 relaxation respectively. As T_{bulk} is in general quite large in comparison to the surface relaxation, the first term can in most cases for porous building materials, like cements, be neglected. Hence the relaxation time can give information on the V/S, which is proportional to the pores size, where the nuclei are present.

In this study an NMR setup was used which is specially designed for measuring ions in porous building materials. This setup makes use of a vertical Oxford 4.7 T superconducting magnet with a vertical 200 mm bore. As the gyromagnetic ratios and hence the resonance frequencies of the selected nuclei are too far apart to be covered by one insert, a specially designed insert was constructed. This insert is a combination of three RF inserts, which can be moved through the magnet with the help of a 3-stepper motor. In Fig. 1 the principle of the setup is given. There are three separate RF setups corresponding to ^{1}H, ^{23}Na and ^{35}Cl.

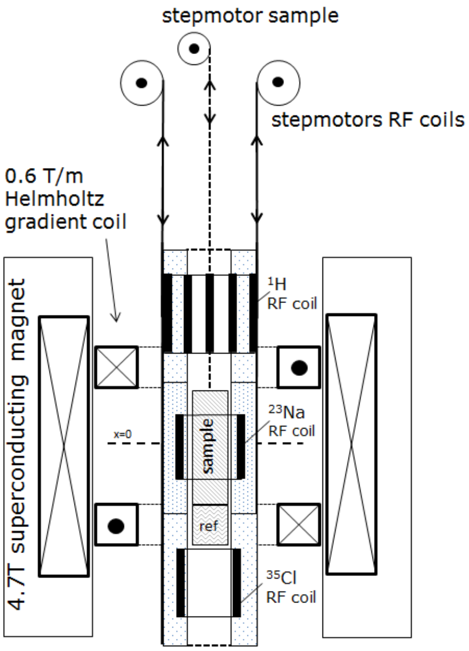

Figure1: A schematic diagram of the NMR setup for measuring the ^{1}H, ^{23}Na and ^{35}Cl signal during the hydration of cement paste. The main field is provided by a 4.7 T superconducting magnet, equipped with an 0.6 T/m anti-Helmholtz gradient coil set. Using a step motor the sample can be moved through the setup.

3. MEASUREMENTS

3.1 Materials

The types of cement used in this study (supplied by HEIDELBERG Group, ENCI B.V. Netherlands) was Ordinary Portland Cement (OPC) which have specific area of 340 m^2/kg In this study the water-to-cement (W/C) was varied from 0.45 to 0.60 at a fixed concentration of 1 M NaCl.

3.2 Hydrogen

The results for the measured longitudinal (T_1) relaxation time and normalized signal of hydrogen as a function of the hydration time are given in Fig. 2. For comparisons we have also shown the results for an experiment for W/C=0.5 made with only water. As can be seen in first order the evolution of the curves in Fig. 2 looks very similar: T_1 relaxation time and the normalized signals of hydrogen first remain stable and after about 1 hour they start to decrease. Whereas the T_1 relaxation time reaches a stable plateau after about 10 hours, the hydrogen signal keeps on decreasing. As can be seen both the T_1 relaxation time and the signals of hydrogen increase with W/C ratio reflecting the increased porosity and pore-size with increasing W/C.

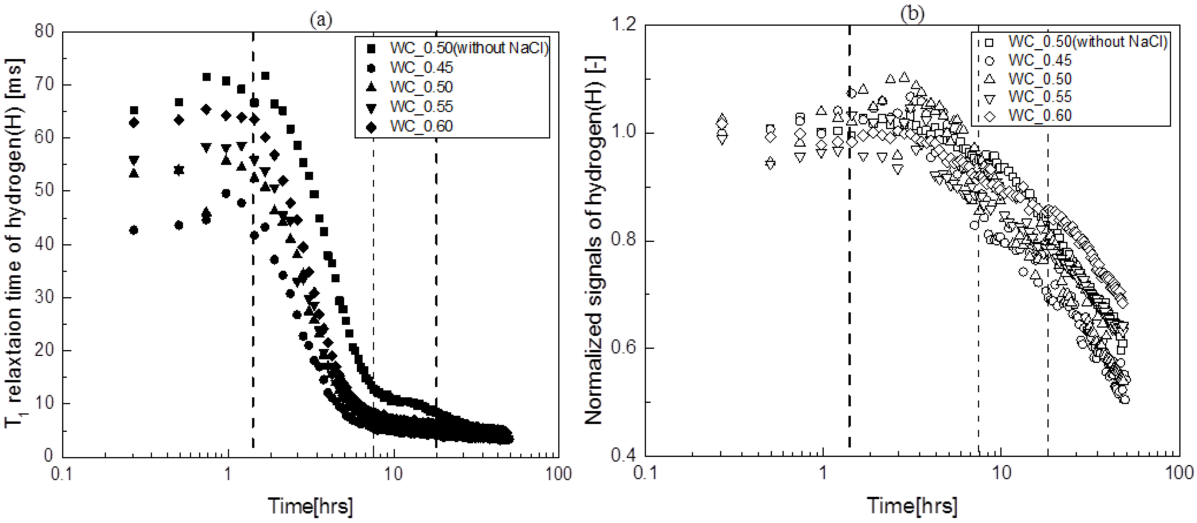

Figure 2: The T_1 relaxation time(a) and normalized signal (b) of hydrogen(H) as the function of time as measured for Portland cements samples with water-to-cement ratio from 0.45 to 0.60 and made with a 1 M NaCl solutions.

Based on the study by P.F. Faure et al.[13], in which they combined NMR and hear flow evolution of hydrating cement, the T_1 evolution correlates with the four stages of cement hydration. The initial reaction and induction period are reflected in the initial constant T_1 relaxation. A second acceleration period where the setting takes place and is reflected in the sharp decrease of the T_1 relaxation. A third stage of deceleration, i.e., the transition from chemical to diffusion controlled reaction, can be observed as the small shoulder as also seen in our experiment with only water. In the final fourth stage the reaction is diffusion controlled and there is a slow continuation of the reaction and the relaxation almost remains constant. These boundaries of the hydration stages are indicated by the dashed lines in the figures.

3.3 Na and Cl

The corresponding measured normalized signals for both Na$^+$ and Cl$^-$ as a function of time are given in Fig 3. Here we have indicated the various stages again in accordance with the T_1 relaxation in time measured for hydrogen.

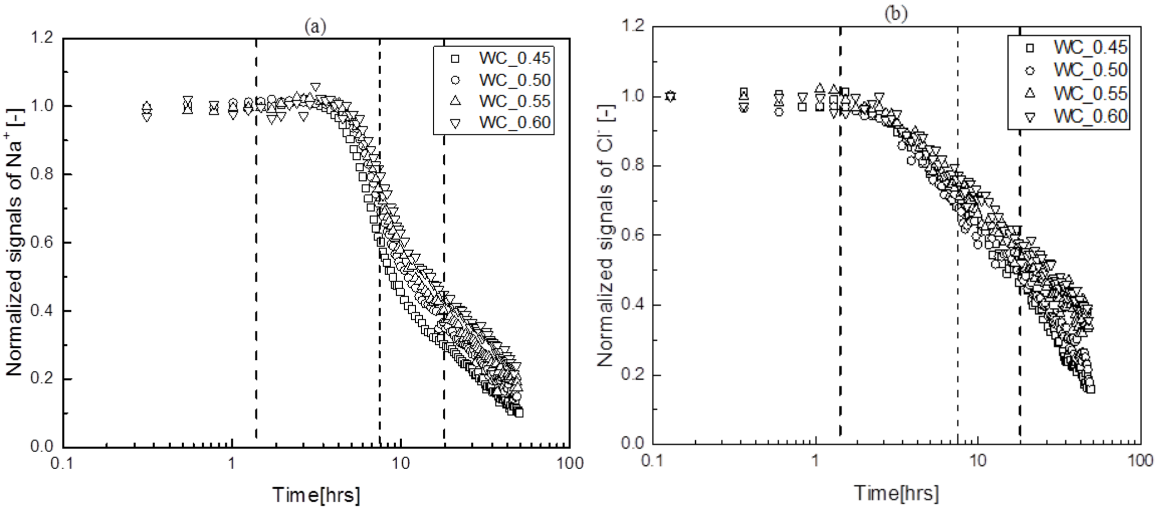

Figure 3: The normalized signals of (a) sodium ions(Na$^+$) and (b) chloride ions(Cl$^-$) as function of time as measured for Portland cements samples with a water-to-cement ratio from 0.45 to 0.60 made with a 1M NaCl solutions.

We can see that with an increase of the W/C ratio of cement paste, i.e., as bigger pores are formed and therefore less surface area, there is less binding of Na$^+$ and Cl$^-$ ions. However if we compare the signal intensity as a function of time, which reflecting the decrease of ion concentration some clear differences between Na$^+$ and Cl$^-$ can be observed. Initially in stage I, i.e., the initial reaction and induction period, the concentration of Na$^+$ and Cl$^-$ remains constant. As soon as stage II, i.e., the acceleration period starts a clear difference can be observed. Whereas the Cl$^-$ concentration immediately start to decrease at the beginning of stage II, for Na$^+$ it is observed that this only starts to decrease near the end of stage II and at the beginning of stage III, i.e., the deceleration stage. In contrast to Cl$^-$ we also observe for Na$^+$ that the decrease in concentration slows down during stage III.

In order to have a clearer understanding of decrease we have plotted in Fig 4 the relationship between the measured Na$^+$ and Cl$^-$ concentration, i.e., we have plotted the normalized measured Cl$^-$ concentration as the function of the normalized measured Na$^+$. As can be seen independent of the W/C ratio all the measurements seem to fall on one master curve. Initially, the Cl$^-$ concentration decreases at first as the Na$^+$ concentration remains constant values (approximately 1.0 M) and then continues to decrease with the decrease of Na$^+$ concentration.

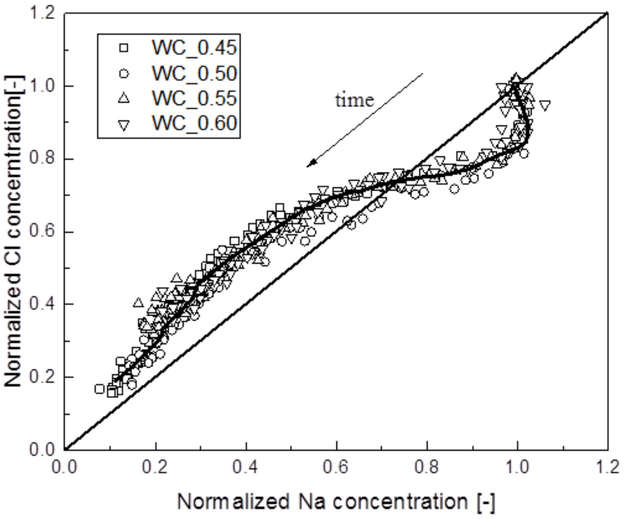

Figure 4: The normalized Cl^- concentration as a function of the normalized Na^+ concentration of cement paste sampled prepared with water-to-cement ratio from 0.45 to 0.60 made with 1 M NaCl solution (see fig 3)

The binding mechanisms for Cl^- can be characterized as both chemical and physical binding [2,3,14]. The AFm compounds ($3CaO \cdot (Al, Fe)_2O_3 \cdot CaSO_4 \cdot nH_2O$) formed during the hydrations are generally known to be able to chemically bind the Cl- ions directly to form Friedel`s salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) [15, 16]. Additionally it is known that the C_3A has a rapid reaction speed in comparison with the other mineral phases (i.e., C_3S and C_2S) and its products include these AFm phases. Also, the Cl^- ions can be physically bound to the porous hydrates, i.e., C-S-H gels can absorb the Cl^- ions on the surface and inside the pores due to its high specific areas [17]. However, it is generally considered there is only as physical adsorption as a binding mechanism for the Na^+. Therefore binding capacity for Na^+ of the sample depends on the hydrate properties (i.e., amount of the porous hydrates and their permeability) formed during hydrations.

The reasons for the observed initial preference for binding of Cl^- (compared with Na^+) could be due to the quickly formed AFm phases (compared with C-S-H phases) during hydration. With the amount of AFm phases decrease and more porous hydrates are formed, the physical binding becomes dominant. Hydrates formed later (after the acceleration period) will bind more the Na^+ ions than the Cl^+ ions in pore solutions.

5. CONCLUSIONS

It has been shown that by using a specially designed NMR setup of the binding of Na^+, Cl^- during can be studied during the hydration of cement pastes made with NaCl solutions. It is observed that the binding of the Na and Cl is closely linked to the hydration process. The initial hydrations could bind more Cl^- ions compared with Na^+ ions during the acceleration period and the later binding preference on Na^+ ions. The increase of W/C ratio results in less binding capability on Na^+ and Cl^- ions.

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