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Abstract

The durability of cement-based materials with respect to exterior aggressions is one of the current priorities in civil engineering. Depending on their use, the cement-based materials can be exposed to different types of aggressive environments. For instance, damages to concrete structures in contact with a saline environment (sea water on bridges, deicing salts on roads, etc.) are of utmost importance. Upon exposure to saline water, Cl^- ions penetrate into the structures and subsequently lead to reinforcement corrosion. Chloride attack is often combined with other aggressive influences such as temperature (e.g., freezing) or the ingress of other ions (e.g., sulfates in sea water). We therefore aim to explore the effect of sodium chloride (NaCl) on the structural chemistry of cement paste.

Existing studies about reinforcement corrosion by chloride have focused on the penetration of Cl^- ions and the comparison between "free" ions (water-soluble ions) and bound ones. However, little is known about the fixation mechanisms, the localization of Cl in the cement matrix and the structural interaction between Cl and the silicate and aluminate hydrate phases present in cement paste. We present here results of a multinuclear nuclear magnetic resonance study on the fixation of chloride in the hydration products and the characterization of new phases potentially appearing due to chloride ingress.

1. Introduction

A quantitative approach to durability is necessary to predict the long-term behavior of concrete structures. Corrosion of steel reinforcement is the major problem when no mechanical solicitations or chemical reactions occur. While sulfates or carbonates can also lead to the deterioration of concrete, chloride is probably the most aggressive and most widespread corrosive ion. It is therefore essential to understand the interactions between chloride and concrete in order to identify and predict all the mechanisms involved. When concrete is in contact with a chloride solution, chloride ions penetrate in the pore solution. They appear in concrete both as "free" Cl^- ions (meaning water-soluble ions) in the pore interstitial solution and as chemically bound component of hydrate phases (e.g., Friedel's salt $Ca_2Al(OH)_6Cl \cdot 2H_2O$ [1]). Free chloride ions are the most dangerous because of their capacity to diffuse towards the steel bars [2].

Interactions between chloride and concrete can be explored by different ways. Studies on the kinetics of chloride ingress by natural diffusion, migration under an electrical field or microstructural characterization are usual methods [3,4]. In this paper we propose to explore these interactions by using nuclear magnetic resonance (NMR). Nuclear magnetic resonance is well known to the study of the microstructure of cement-paste materials. Concerning the binding of chloride, few works exist and most of them are ^{27}Al studies [5]. The lack of ^{35}Cl NMR reference studies [6–8] is an obstacle for the comprehension of chloride binding in concrete.

A two-step approach is conducted here to study the interactions between chloride and cement-paste hydrates. First, the modifications of the hydration kinetics in

presence of chloride are determined by the evolution of both the longitudinal relaxation rate ($1/T_1$) and the NMR-detectable amount of chloride with hydration time are explored. And on the other hand, ^{29}Si, ^{27}Al and ^{35}Cl NMR spectra of hardened materials are presented in order to identify possible modifications of the microstructure. These spectra were obtained on different Bruker spectrometers operating with field of 2.85, 7.0, 11.7 and 19.6 T.

2. Modifications of the hydration kinetics

The intrusion of chloride in a cement-paste material usually results from the contact with a saline solution. In the experiments presented here, the presence of chloride was achieved by direct addition of chloride to the pastes. The ratio (mass of NaCl)/(mass of cement) is 3% and the water/cement (w/c) ratio is 0.35 in all the tested materials. The freshly prepared pastes were put into 8-mm-diameter 1-cm-length static tubes for the T_1 longitudinal relaxation time and spectral measurements realized at different hydration times. We tested three different materials: two cement pastes named HTS and Le Havre containing 4% and 10% of C_3A (calcium aluminate: $3CaO \cdot Al_2O_3$), respectively (the rest of the chemical composition is the same), and a pure C_3S paste (calcium silicate: $3CaO \cdot SiO_2$).

In Fig. 1, ^{23}Na NMR spectra measurements measured at 2.85 T on a HTS cement paste are presented. The longitudinal relaxation rate $1/T_1$ and the detectable sodium amount evolve in three steps:

– Until a hydration time of 200 min, both the amount of detectable sodium and the relaxation rate are constant; the observed relaxation behavior in this time interval is monoexponential.
– From 200 to ~10000 min (~7 days), the relaxation rate is divided in two components; one is attributed to the bulk Na$^+$ ions (from 500 to 2500 s^{-1}) and the other one to the Na$^+$ ions at the surface of the material (from 500 to 30000 s^{-1}). During this 5-day period, the amount of detectable sodium decreases from 100% to ~20%.
– After 7 days, both relaxation rate and amount of detectable sodium are roughly constant.

This result suggests that there is no specific interaction between the sodium ion and the hydrating cement. The decrease in the amount of detectable sodium is due to its confinement in progressively smaller pores during the course of the hydration process.

In a second experiment, the kinetics of the hydration process was studied by ^{35}Cl NMR. A comparison of the results obtained for the cement pastes (the curves for HTS and Le Havre were obtained at 2.85 and 7 T, respectively) and a C_3S paste (measured at 2.85 T) is given in Fig. 2. The kinetics for the HTS cement and C_3S cement is quite similar and three periods can be identified:

– Until 250 min, the amount of detectable chloride and the relaxation rate are constant.
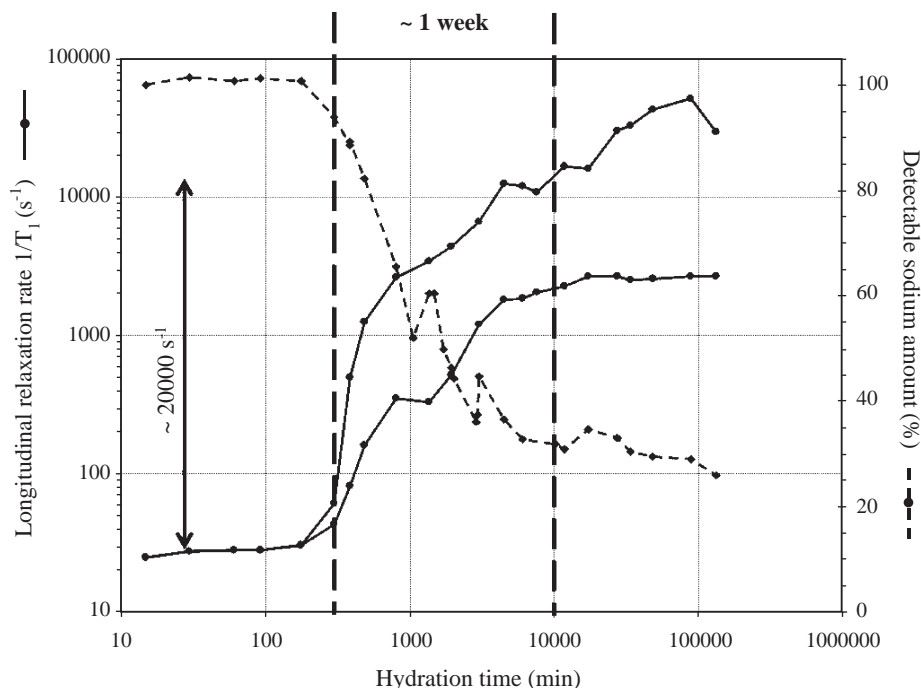– From 250 to ~500 min (~8 h), only one relaxation rate is obtained varying from 60 to 600 s^{-1}. This

Fig. 1. ^{23}Na kinetics of hydration for a cement paste (w/c=0.35) with an addition of 3% NaCl in mass of cement. After the onset of the hydration process, two relaxation rates are observed: one can be attributed to the Na$^+$ ions in the pore volume and the other to the Na$^+$ ions adsorbed at the surface of the material. The decrease of the amount of detectable sodium is due to its confinement into smaller and smaller pores over the course of the hydration process.
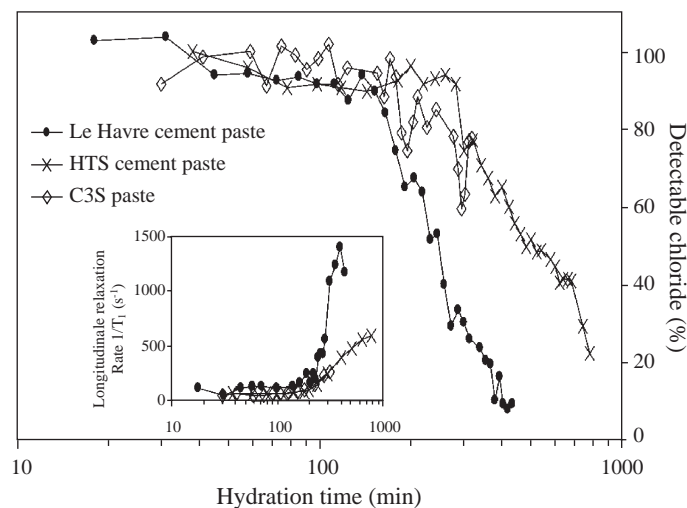
Fig. 2. ^{35}Cl kinetics of hydration for a cement paste ($\times$ for HTS and $\bullet$ for Le Havre) and a C_3S paste ($\diamond$) produced with an addition 3% of NaCl in mass of cement (w/c =0.35). Compared to the ^{23}Na kinetics, the decrease in detectable ^{35}Cl occurs faster and the increase of the relaxation rate is less pronounced. From the ^{35}Cl point of view, the amount of C_3A is determinant respect to the hardening process.

relaxation rate is very low compared to those obtained for ^{23}Na measurements or ^{1}H ones [9]. The hardening process is not visible from the relaxation rate data ($1/T_1$ varies from ~50 to ~500 s^{-1}). On the other hand, the amount of detectable chloride decreases from 100% to ~20% during 5 h.

– After 8 h of hydration, the relaxation rate seems to become quite constant whereas chloride becomes undetectable for the C_3S material.

For Le Havre cement, the decomposition is the same but the hydration process is faster (150 min) because of the low

amount of C_3A and the longitudinal relaxation rate variation is higher (from ~100 to ~1200 s^{-1}) than the one for the HTS cement paste. On the other hand, C_3S paste, containing no C_3A, has a kinetics closer to the HTS cement.

At this point, it seems that the most important effect on sodium behavior is its confinement in the pores during the hardening process; whereas for chloride, chemical reactions are probably the most important reason of its faster disappearance. Moreover, from a ^{35}Cl point of view, the higher the amount of C_3A is, the faster the hardening process is. The hardening time is lower when the amount of C_3A is higher (150 min for Le Havre instead of 250 min
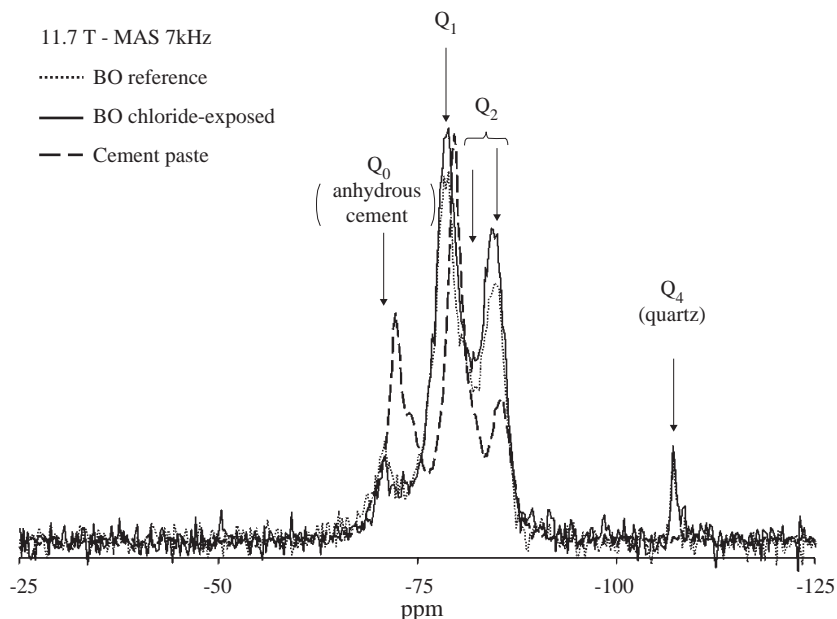

Fig. 3. ^{29}Si spectra of the BO reference concrete (dot line) and the chloride-exposed sample (full line) at 11.7 T. The comparison between the chloride-treated and the reference samples shows a rehydration of previously unreacted anhydrous cement due to the chloride exposure.

for HTS) and especially the increase of the relaxation rate $1/T_1$ is much higher (1300 s^{-1} for Le Havre instead of 500 s^{-1} for HTS).

In order to gain further insights into the interactions between chloride and the cement matrix, high field spectra are realized on cement paste as well as on older concrete.

3. Spectroscopic studies on the effect of chloride exposure

Two kinds of materials have been studied. The first one was a 28-day-aged HTS cement paste with a ratio w/c=0.35 and hydrated directly with a solution containing 3% of NaCl in mass of cement. The other material was an ordinary concrete (named BO) obtained by mixing sand, aggregates and the same cement as in the paste with a ratio w/c=0.5. After 213 days of hydration and vacuum water diffusion, a 10-cm-height 11-cm-diameter cylinder of this concrete was put in contact for 61 days with a basic solution of NaCl/NaOH (30 and 4 g/L, respectively) to match the pH of the interstitial solution of the material. Finally, the concrete cylinder was stored at ambient conditions for several weeks.

Different nuclei were studied to explore the possible interactions between chloride and the material.

3.1. ^{29}Si MAS NMR

^{29}Si experiments at 11.7 T have been performed on samples of the BO concrete non-altered and altered by the NaCl/NaOH solution. The resulting spectra for the concrete samples as well as for the cement paste are shown in Fig. 3. One observes that the Q_0 contribution for the chloride-exposed sample decreases whereas the Q_1 and Q_2 ones

increase. From these quantitative spectra, the mean length l of tetrahedral chains can be determined ($l=Q_2/Q_1$) as well as the mean percentage of hydration phases ($C_{hyd}=Q_1+Q_2$). For the reference sample, we obtain $l=0.77$ and $C_{hyd}=87\%$, and for the chloride-exposed sample $l=0.76$ and $C_{hyd}=94\%$. Moreover, the decrease of Q_0 contribution is about 10%. Concerning the cement paste, the spectrum is dominated by a large contribution Q_0 of nonhydrated cement ($C_{hyd}=69\%$) and a more prominent contribution of Q_1 respect to Q_2 ($l=0.65$).

The length of the siliceous chains is not notably affected by the chloride exposure. The main effect of the treatment with saline solution is therefore the hydration of unhydrated cement still present in concrete.

3.2. ^{27}Al MAS NMR

The same kind of comparison has been made for the ^{27}Al nucleus. The results, including the cement paste spectrum, are shown on Fig. 4. The BO concrete spectra were recorded at 11.7 T whereas the cement paste was measured at 19.6 T. Two contributions can be observed. Between -10 and 25 ppm, the octahedral group corresponds to the aluminate hydrates; its main components are AFm (monosulfoaluminate), AFt (trisulfoaluminate) and (in the chloride-exposed samples) Friedel's salt [5] as well as a peak due to hydration (aluminum in octahedral position instead of calcium). The signal due to tetrahedral groups observed between 50 and 100 ppm corresponds to aluminum incorporated into the C-S-H or to Al contained in still unhydrated cement.

Three effects are observed upon contact with the saline solution. First, the increased amount of hydrates indicates
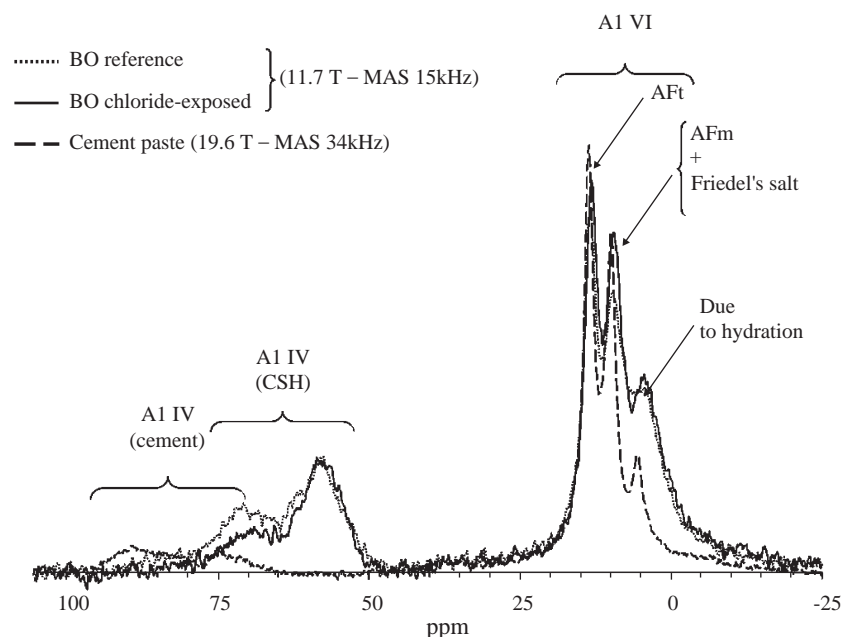

Fig. 4. ^{27}Al spectra of the concrete BO reference sample (dotted line) and the chloride-exposed sample (full line) at 11.7 T and the ^{27}Al spectrum of the cement paste (dash line) at 19.6 T. Exposure to chloride leads to the formation of Friedel's salt. Al IV modifications appear when the concrete is in contact with a saline solution. Al IV for the cement present only the characteristic of aluminum incorporated in the cement.
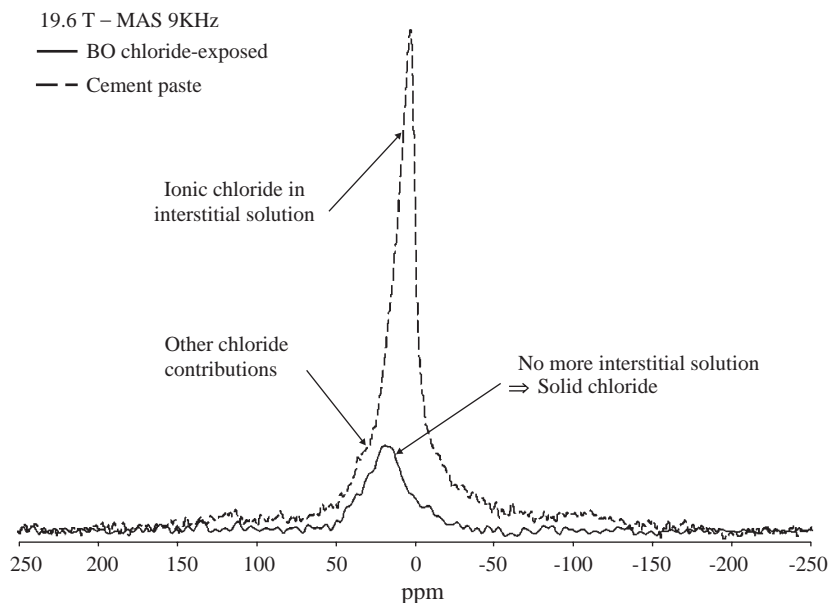
Fig. 5. ^{35}Cl spectra of the concrete BO chloride-exposed sample (full line) and the cement paste (dash line) at 19.6 T. The cement paste spectrum is the superposition of one peak near 0 ppm (ionic chloride) and another one near 30 ppm (solid or adsorbed chloride). The concrete spectrum exhibits only the solid (attributed to Friedel's salt) and the adsorbed chloride contribution.

the rehydration of the residual cement. Then, we observe the apparition of Friedel's salt and the disappearance of a part of AFm hydrates [10]. Finally, in the tetrahedral group, a peak decreases when another one increases. In the cement paste spectrum, if Friedel's salt presence is detected, there is no contribution coming from aluminum substituted in the C-S-H but only from the one substituted in the residual cement.

This observation confirms the rehydration of the cement when the concrete is exposed to NaCl solution. Moreover, the presence of Friedel's salt indicates the nature of the chemical reaction between chloride and aluminum while no specific reaction products could be identified in the silicon spectra.

3.3. ^{35}Cl MAS NMR

To conclude the structural exploration, ^{35}Cl experiments at 19.6 T have been performed on the cement paste and the chloride-exposed concrete (Fig. 5). The cement paste spectrum is a superposition of two contributions: one near 0 ppm coming from ionic chloride and the other one near 30 ppm corresponding to solid or adsorbed chloride. On the other hand, since no capillary water and no free ionic chloride are present, the concrete spectrum reflects only the solid or adsorbed chloride contribution. This spectrum can be plausibly attributed to Friedel's salt and adsorbed chloride. But this last result should be evaluated further to confirm these results.

4. Conclusion

Nuclear magnetic resonance is a powerful tool for probing the interactions between chlorides and cement hydrates. Both kinetic and spectroscopy experiments have

been performed for different nuclei (^{29}Si, ^{27}Al and ^{35}Cl). While sodium does not seem to be affected by the hydration process, chloride disappears very fast due to chemical reactions with components of the cement. ^{27}Al and ^{29}Si spectroscopy proved that only aluminum interacts with chloride and that the exposure of concrete to a NaCl solution leads mainly to a rehydration of residual cement without affecting the structure of the C-S-H product. ^{35}Cl spectroscopy showed the absence of ionic chloride when the material is dried. Only solid or adsorbed chloride is observed in this chloride-treated concrete material. The next step of our studies will be the understanding of the different mechanisms involved in the chloride/aluminate formation upon exposure of the material to a saline solution.

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