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Detection of free chloride in concrete by NMR

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Abstract

Laboratory experiments to detect chloride in a cement matrix using pulse nuclear magnetic resonance (NMR) were conducted. The coils were in the centimeter scale and the magnetic field was 2.35 T. NMR signals were obtained from both aqueous chloride solution and samples of both regular and white Portland cement (WPC). A concrete sample from a sidewalk that had been in the field for 20 years was also tested. The experiments demonstrated that the signal-to-noise ratio (SNR) for a centimeter-scale cement sample volume is so small, even after averaging, that sample volumes much lower than that are unlikely to produce measurable signals at fields of 1 T or below. The consequence is that the potential for realizing an embedded NMR-based sensor including the magnet is low. Parametric studies identify feasible alternative coil diameters and magnetic field strengths for detecting chloride ion concentrations in hardened concrete.

Keywords: Cement; Chloride; NMR

1. Introduction

Chloride ions used in deicing agents applied to reinforced concrete corrode the embedded steel and thereby threaten concrete-based civil infrastructure, such as bridges, roads, and parking structures. In fact, the intrusion of chloride ions is the major cause of deterioration of these structures. Corrosion of embedded steel reinforcement in concrete occurs after the level of chloride ions in the concrete in the vicinity of the embedded reinforcement reaches 0.2%. Depending on the exposure environment, depth of the embedded reinforcement, and the quality of the concrete, corrosion in concrete infrastructure can begin as early as the first few years to as late as 25 years in the life of a structure. Thus, a sensor that would report chloride levels from the interior of concrete structures is needed. An embedded nuclear magnetic resonance (NMR) that determines chloride levels in concrete would be an especially attractive solution to the problem because NMR is quite specific in its identification of chloride; also, since there is no chemical interaction of the device with the chloride, it could be easily designed to operate for the predicted lifespan of the structure.

1.1. Role of chlorides in the infrastructure

Corrosion of the civil infrastructure (bridges, roads, parking facilities) is a costly consequence of keeping the infrastructure operating during winter. Although Portland cement-based concrete used to build the infrastructure provides a passivating environment for the embedded steel reinforcement, thus protecting it from corrosion due to exposure to moisture and oxygen [1], the entry of chloride ions into the concrete initiates corrosion of the steel.

Although chloride has been used as a purposeful admixture in the form of calcium chloride for its set and strength accelerating properties, its role in corrosion of embedded steel reinforcement has all but eliminated its use as a set accelerator for public and significant private infrastructure. Chloride also occurs in insignificant amounts in potable water, aggregates, and admixtures used in concrete, but these sources of chloride are usually insignificant due to the stringent restrictions placed on the chloride content of admixtures for use in important structures. The most signif-

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icant source of chloride that causes corrosion of steel in the infrastructure is from chloride-containing deicing agents used to melt snow and ice and keep the infrastructure clear. The intrusion of chloride into the concrete occurs over a prolonged period. Specifications on the required amount of concrete cover over embedded reinforcement depend principally on the potential exposure to chlorides. The depth of the reinforcement from the exposed surface and the quality of the concrete along with the frequency and duration of exposure determine the time required for chlorides to reach embedded steel in quantities sufficient to initiate corrosion.

This time-to-corrosion parameter for embedded steel reinforcement is the determiner of the life of a structure. Numerous studies have been undertaken to study the time-to-corrosion with respect to concrete quality, exposure, and initial chloride levels in the concrete. In these studies, as well as in the everyday maintenance of the infrastructure, the chloride content and concentration profile are measured by crushing concrete samples and evaluating the extracted chlorides through wet chemistry. These methods determine the chloride content by weight based on the concrete sample itself. These tests are typically performed during the later ages of a structure when it is approaching the end of its predicted lifespan or when evidence of deterioration indicates a potential corrosion problem. Other methods of detecting the initiation of corrosion also have been devel-

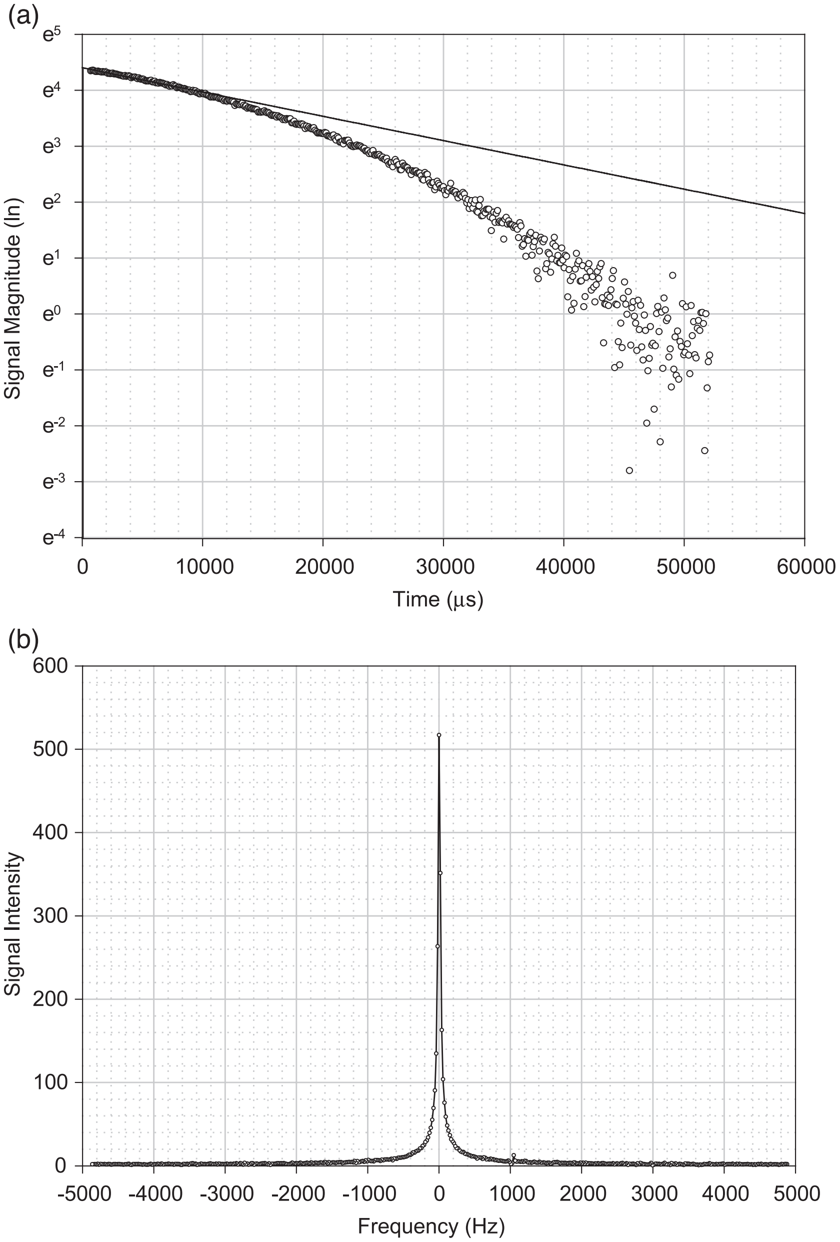


Fig. 1. (a) FID of 1.1 M aqueous chloride solution after 1024 averaged signals. The line is a log-linear fit to the earliest points. The spin–spin relaxation time T_2^* calculated from the slope of the line was 23 ms. (b) Fourier transform of the data. SNR = 181.

oped. These methods do not detect or depend on a parameter such as chloride content to determine the corrosion potential, but detect when corrosion is actually occurring. Although the chloride content of the concrete is not the only parameter that determines when corrosion will begin, it is the one parameter that is well established as a major contributor to corrosion.

1.2. Characteristics of an embedded NMR device

NMR can, in principle, determine the presence and concentrations of chloride. NMR is the phenomenon by which a signal is generated when nuclei having nonzero nuclear spin undergo transitions between energy states. A magnetic field, B_0, aligns the magnetic moments of the nuclei, which precess around the direction of the applied field. Excitation of these moments with electromagnetic radiation of a frequency characteristic of the species of interest causes energy transitions that are detectable. The presence of measurable transitions at known frequencies is a diagnostic of the presence of the species. Chlorine has a nonzero spin, 3/2 in its most abundant isotopes. Thus, chlorine is detectable in principle with NMR. The major components of any remotely deployed NMR sensor are a permanent magnet designed to provide a uniform magnetic field (B_0), a coil that both generates a small excitation magnetic field (B_1) in the sample and receives the signal back from the sample, and electronic components for filtering, mixing, digitizing, and summing the readings taken from the coil. The important and interesting question is whether a compact system incorporating all of these functions can be expected to detect chloride in concrete.

The sample volume is most critical because it governs the number of atoms one can expect to be present. For deployment in concrete infrastructure, the overall system must have a characteristic length scale of less than 5 cm on a side, which is close to the maximum size of coarse aggregate in concrete. A magnetic field of 7–19 T typically is used to obtain a signal; a potential in situ NMR sensor, however, would be limited by available permanent magnet materials to 1 T or less. The magnet occupies much of the volume of the device because it must deliver both a maximum field strength and good uniformity. The solenoid coil connected to the electronic chip might have a diameter of 2–4 mm and would be placed in the barrel of the specially designed permanent magnet. Fundamental calculations of the field homogeneity inside such a package probably constrain the sample size to 1 mm^3. Thus, the research question becomes whether one can reasonably expect to detect chloride in a volume of characteristic dimension 1 mm with a magnetic field strength less than 1 T.

1.3. Previous study of cementitious materials using NMR

Although NMR has been used in cement and concrete research since the early 1980s, chloride (^{35}Cl and ^{37}Cl) has been rarely studied due to its low sensitivity. Most chloride-related studies have been made with ^{27}Al NMR because aluminum is 100% abundant and has a higher sensitivity than chlorine, and the amount of free chloride ions in Portland cement concrete is inversely proportional to the amount of tricalcium aluminate and tetracalcium aluminoferrite [1–3]. Kirkpatrick et al. [4,5] and Yu and Kirkpatrick [6] reported on ^{35}Cl NMR studies for cement research. Their studies were based on suspensions, however, and not cured cement. More recently, Cano et al. [7] investigated the penetration of chloride into mortar with two water-to-cement ratios. They used a high concentration of chloride to aid detection. The relatively open structures admitted the chloride over a period of hours, much faster than explained by diffusion; they concluded that advection along pores was the mechanism of penetration.

1.4. Purpose of this work

The purpose of this work was to investigate the detection of chloride by NMR in concrete at low concentrations to provide the knowledge necessary to decide if NMR based sensing of chlorides in concrete is feasible and at what scale. The studies were confined to chloride concentrations of 2% by weight of cement or less. We experimented with chloride in aqueous solution, in laboratory-prepared cement samples, and in a sample of concrete that had resided for two decades in the field. This work also concentrated on scaling the coil and magnetic field strength with respect to the required sensitivity of the device. Since signal-to-noise ratio (SNR) is a standard measure of the performance of an NMR system, the feasibility of chlorine detection can be determined using the SNR calculated with the model of Peck et al. [8]. The measured SNR for the various chlorine concentrations and

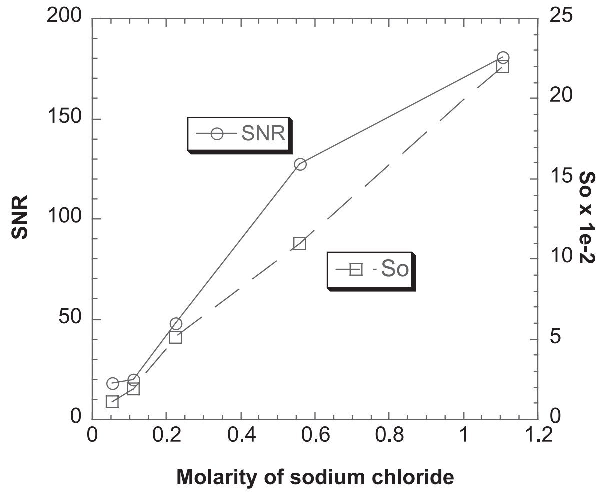


Fig. 2. Values of the SNR of the NMR signal obtained by applying Eq. (1) to the Fourier transform of the data for the aqueous chloride samples. Also shown is the quantity S_0 that should be proportional to the number of spins present. As expected from NMR theory, the number of spins is proportional to the concentration for samples of constant volume.

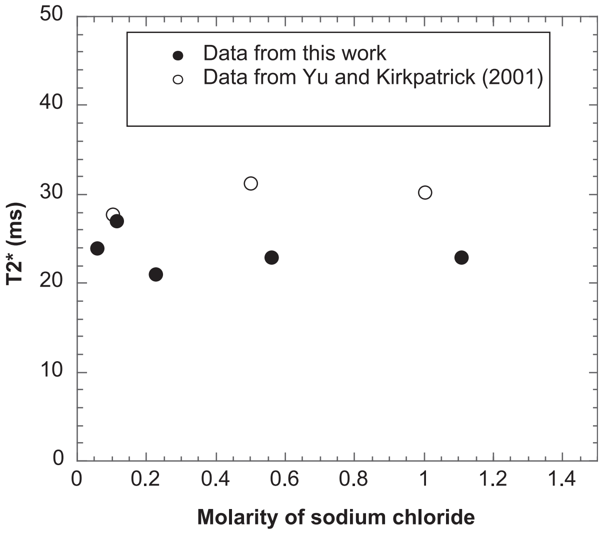


Fig. 3. Values of the spin–spin relaxation time are shown as a function of sodium chloride concentration. Also shown are data from Yu and Kirkpatrick [6] also in a 2.35-T magnet. The values from this work and theirs agree within about 20%.

samples types formed the foundation of a parametric study to assess the coil size and magnetic field strengths required to detect chlorine in Portland cement concretes.

Details of the experimental program and its results are presented. A parametric study was then performed using the results of the experimental program to establish the validity of assumptions concerning a hypothetical embedded device to detect chlorides in concrete and to predict requirements of a device based on the experimental data. The feasibility of such a device is discussed in light of the experimental data presented and further parametric studies to assess coil dimensions and magnetic field strengths required to detect chlorides in hardened Portland cement concrete.

2. Experiments

The first experiments were performed on aqueous solutions of sodium chloride that was chosen as the test source of chloride because it reacts less with the host cement than calcium chloride that was used in the past as a setting agent [9–11]. A series of solutions having concentrations between 0.055 and 1.1 M sodium chloride were prepared and tested to establish baseline SNR for chloride in the NMR system being used. These concentrations were selected so that the total number of spins present in these solution samples corresponded to the number of spins used later in the cement

Table 1
The NMR response of aqueous solutions of sodium chloride

Concentration (%)[a]	Peak (s)	SNR	T_2^* (ms)	$S_0 \times 10^{-3}$
0.1	27.3	17.9	24	1.1
0.2	52.6	19.7	27	1.9
0.4	107	47.9	21	5.1
1.0	255	127.5	23	11
2.0	517	181	23	22

[a] Percentage of chloride content by weight of Portland cement to be used in other experiments.

Table 2
NMR responses of freshly mixed WPC, NaCl, and water

Sample[a]	Hours after mixing the sample					
	3 h	6 h	12 h	24 h	36 h	48 h
W: 0.1%	3.3 s	[b]	[c]	[c]	[c]	[c]
	5.4					
	1.1 ms					
	5.3					
W: 0.2%	3.3	[b]	[c]	[c]	[c]	[c]
	5.4					
	2.0					
	2.3					
W: 0.4%	7.0	2.9	[b]	[c]	[c]	[c]
	11	6.7				
	1.5	1.2				
	7.1	1.4				
W: 1.0%	16	7.1	3.8	2.9	[b]	[c]
	27	14	5.6	4.5		
	1.9	1.0	1.7	1.2		
	12	13	3.2	4.1		
W: 2.0%	41	19	6.4	4.6	3.3	3.44
	45	26	10	9.3	5.3	6.7
	1.9	1.1	1.1	0.96	1.0	0.7
	30	30	10	9.2	6.1	12

One thousand and twenty-four signals were averaged in each case. The quantities listed are peak value of the Fourier transform (s), SNR, T_2^* (ms), and ($S_0 \times 10^{-3}$) for ^{35}Cl.

[a] Percentage of chlorine content by weight of Portland cement in sample.

[b] No signal detected.

[c] No test.

Table 3
NMR responses of freshly mixed GPC, NaCl, and water

Sample[a]	Hours after mixing the sample					
	3 h	6 h	12 h	24 h	36 h	48 h
G: 0.1%	[b]	[c]	[c]	[c]	[c]	[c]
G: 0.2%	[b]	[c]	[c]	[c]	[c]	[c]
G: 0.4%	3.1	1.7	[b]	[c]	[c]	[c]
	7.4	2.9				
	0.71	0.53				
	11	10				
G: 1.0%	3.7	2.0	[b]	[c]	[c]	[c]
	11	2.7				
	0.61	0.57				
	17	11				
G: 2.0%	15	11	6.4	3.78	3.2	2.05
	22	14	9.1	6.1	6.1	2.9
	0.68	0.59	0.45	0.66	0.46	0.5
	55	54	57	15	27	14

One thousand and twenty-four signals were averaged in each case. The quantities listed are peak value of the Fourier transform (s), SNR, T_2^* (ms), and ($S_0 \times 10^{-2}$) for ^{35}Cl in each case.

[a] Percentage of chlorine content by weight of Portland cement in sample.

[b] No signal detected.

[c] No test.

samples. Instrument settings and procedures were established that yielded a robust signal from dilute aqueous solutions of sodium chloride.

Freshly mixed neat (water and cement) white Portland cement (WPC) samples containing from 0.1% to 2.0% atomic chloride by weight of cement were investigated in the second suite of experiments. We mixed the chloride directly with the cement paste and water from the start of the experiment to ensure that chloride was present throughout the sample. Some of the chloride is bound into the cement during hydration, but Al-Hussaini et al. [11] showed that approximately half of added chloride, especially sodium chloride, remains water soluble in the range of 0–2% of chloride by weight of cement. Thus, the loss of some chloride to the matrix was accepted in return for assurance that chloride was present throughout the cement. WPC was used initially because it contains almost no iron bearing compounds. The strength of the paramagnetic effect of the iron in gray Portland cement (GPC) is not well established for experiments of this type. Therefore, WPC was used to minimize this potential effect on the SNR. All samples were prepared with a water-to-cement ratio of 0.5; they were capped in bottles after preparation and maintained in that condition at all times. Their NMR response was measured at

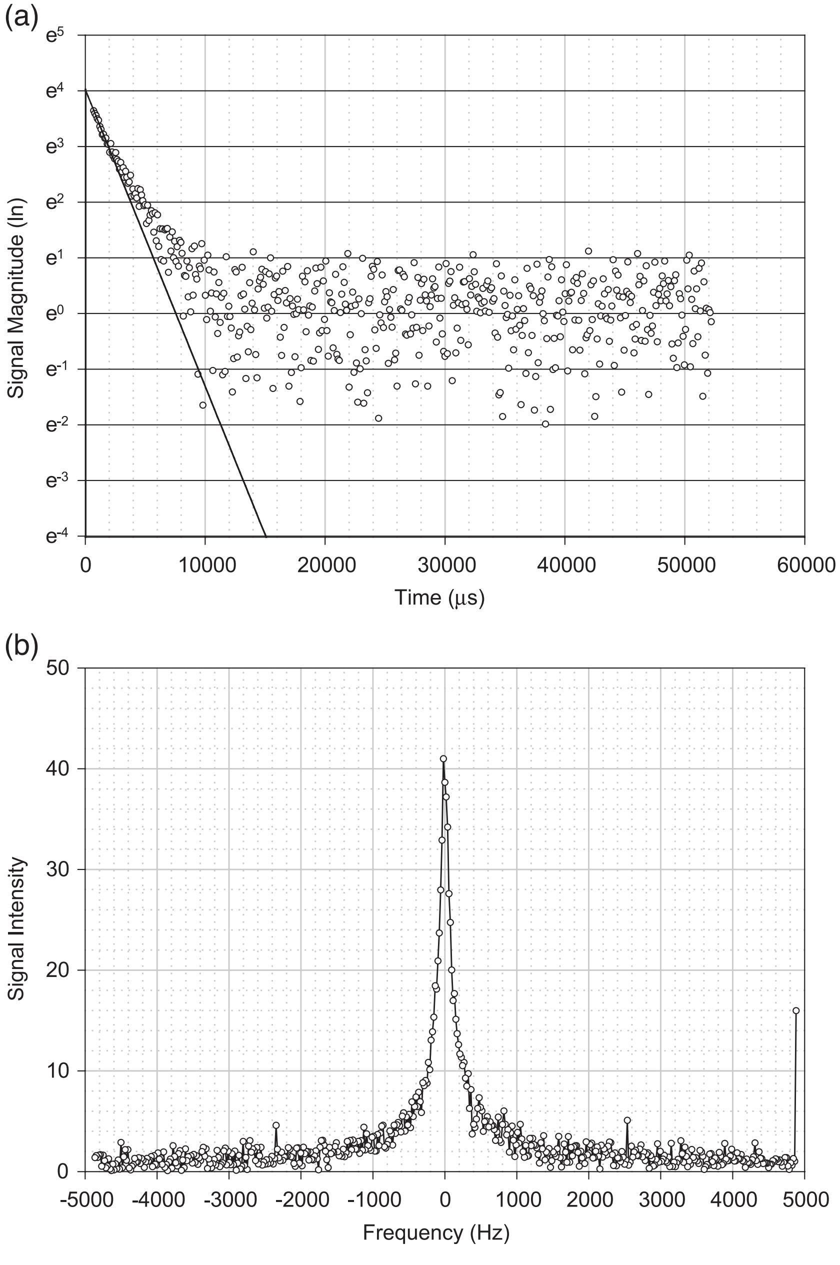


Fig. 4. (a) FID of chloride in hydrating WPC 3 h after mixing, based on 1024 averaged signals. The chloride concentration was 2% by weight of cement. The line is the log-linear fit to the early points. T_2^* was calculated to be 1.9 ms (b) Fourier transform of the data. SNR = 45.

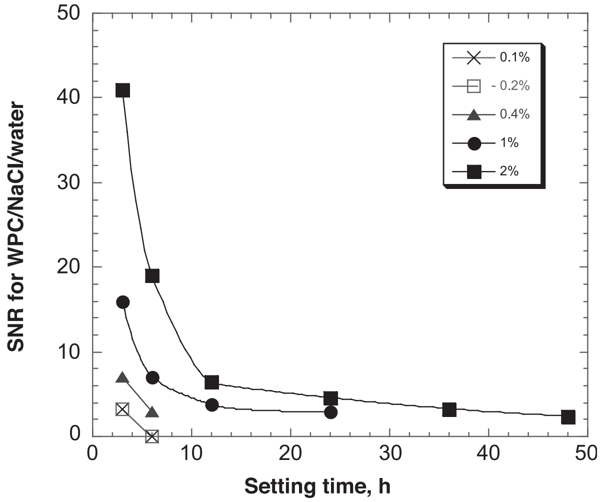


Fig. 5. The decay of chloride SNR obtained from hydrating WPC with indicated amounts of NaCl admixture. The SNR decayed precipitously in the first 12 h. Collecting 1024 signals and averaging them was not sufficient to detect a signal from the two lowest concentrations after 6 h.

3, 6, 12, 24, 36, and 48 h after mixing. GPC samples were then prepared in a similar manner to the WPC samples and tested.

The effects of diluting the neat cement samples with a known quantity of fine aggregate with a known composition were then investigated. The aggregate produced a more porous solid that was better suited to subsequent drying and rewetting experiments. WPC, water, sodium chloride, and fine uniformly graded quartz sand were prepared and tested. The chloride mass was 2% of the mass of cement used in the experiment. A sample from this batch was dried, rewetted, and remeasured for the presence of chloride.

Finally, a cured and aged (20-year-old) sample of concrete from pavement was tested for the presence of chloride using the NMR system. Wet chemical methods were used to determine the gross chloride content of the sample from which the smaller sample used in the experiment was taken.

All the samples were tested with an in-house-made NMR probe, which has a solenoid coil of 21 turns, 3.5 cm height, and 1.5 cm diameter. The resonance frequency of the probe was tuned to 9.7923974 MHz to detect ^{35}Cl signal in a 2.35 T magnetic field. The Q factor of the sample probe was 50 when the sample was placed in the coil. Then the sample and NMR probe were placed in a 2.35 T superconducting magnet. An Apollo NMR spectrometer manufactured by Tecmag detected the chloride in the experiment. NMR software, NTNMR, also by Tecmag, controlled the spectrometer and acquired the signal. The 90° pulse duration was 32.5 μs. The number of acquired data points was 256 with a dwell time of 125 μs, which represented a sampling rate of 8.0 kHz. Thus, the acquisition time for one reading was 32 ms. The data acquisition began 625 μs after the end of the RF pulse to avoid the transmitter/receiver transient response (or artifact).

3. Results

We report sample free induction decays (FID), their Fourier transforms, the SNR, and apparent spin–spin relaxation times T_2^* as the primary results of the experiments. The SNR was calculated from the Fourier transform of the FID according to Eq. (1).

$$\mathrm{SNR} = 2.5[\text{signal peak/peak} - \text{to} - \text{peak noise}] \qquad (1)$$

where the peak-to-peak noise means the difference between the highest peak and the lowest valley in the noise signal. This method follows ASTM standard E386-90. The relaxation times were calculated by fitting the exponentially decaying signal to a straight line on a semilog plot.

A representative FID and its Fourier transform for a 1.1-M chloride solution appear in Fig. 1. After 1024 measurements, the peak signal from the Fourier transform was 517 (a.u.), the SNR was 180, and T_2^* was 23 ms. SNR found for all investigated aqueous concentrations appear in Fig. 2. The SNR decreased from 180 for the 1.1-M solution to 18 for the 0.055-M solution. Measured values of T_2^* appear in Fig. 3 in comparison to the results of Yu and Kirkpatrick [6]. Table 1 contains numerical values for the peak of the transform, the SNR, and T_2^*.

Results for the premixed samples of cement, water, and sodium chloride appear in Figs. 4–6 and Tables 2 and 3. The FID and associated Fourier transform for the 2% chloride (by mass of WPC) 3 h after mixing appear in Fig. 4a and b. The number of averages was the same as for the aqueous solutions. The signal strength was 41, the SNR was 45, and T_2^* was only 1.88 ms, an order of magnitude

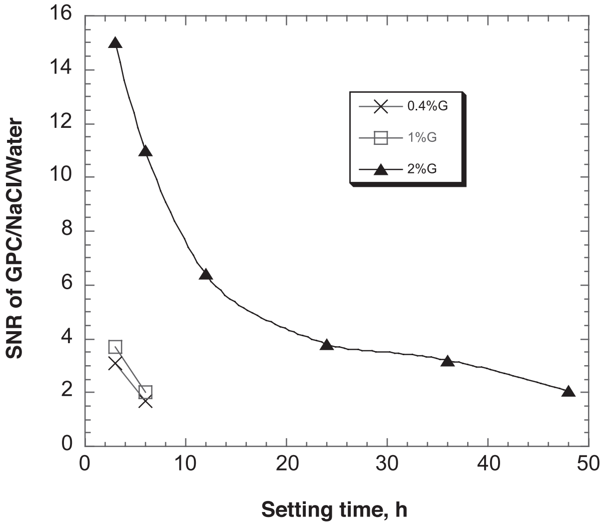


Fig. 6. The decay of chloride SNR obtained from hydrating GPC with indicated amounts of NaCl admixture. The SNR decayed precipitously in the first 12 h. Collecting 1024 signals and averaging them was not sufficient to detect a signal from the two lowest concentrations at all and no signal was detected from the 0.4% and 1% samples after 6 h. The use of GPC made the chloride more difficult to detect.

Table 4a
SNR of samples of cured WPC mortar mixed with NaCl, before oven drying

Sample	Weight (g)	Cl by weight Portland cement (%)	Estimated chlorine weight (mg)	NaCl weight (mg)	Cement weight (g)	Water weight (g)	Curing time (days)	SNR	Average SNR	STDV
WPM-1	5.3	2.0	0.03	0.049	1.5	0.75	16	11.4	9.2	2.0
WPM-2							26	7.4		
WPM-3							55	8.9		

reduction from the aqueous case. A summary plot of the SNR as a function of time for chloride in WPC appears in Fig. 5. The SNR declined over the first 20 h and then less precipitously over the next 50 h. In cases where it was measurable, 0.4% and greater, T_2^* was typically 2 ms after 3 h and decreased thereafter (Table 2). An analogous plot for GPC appears in Fig. 6. The SNR for GPC in general was lower by an order of magnitude for the same measurement conditions. No signal was obtained after 1024 averages at the two lowest concentrations beyond 3 h. Also, T_2^* never exceeded a millisecond for any of the GPC samples.

The mortar sample (water, WPC, sand, sodium chloride) was allowed to cure over a period of 26 days while its NMR response was measured (Table 4a). The resulting time record of SNR after 131,032 averages of the signal appears in Fig. 7. After 26 days, the SNR decreased from over 300 to 7.4. The moisture content of the sample was determined to be 11.6%. The sample was then oven dried for 3 days, after which the sample was unresponsive to excitation. The sample was then placed in a humid atmosphere and tested after 1, 6, and 13 days of exposure to a humid environment. The SNR was restored to its value of 7.4 after 2 weeks of exposure, during which the moisture content was restored to 6.95% (Table 4b). A one-dimensional water NMR image of the mortar sample appears in Fig. 8 for three stages of the experiment: after curing, after drying, and after 2 weeks of rewetting.

The fourth test was an attempt to measure chloride in a field sample of sidewalk concrete that had been exposed to chloride periodically for ice control over 20 years. The sample was known to contain 0.007 g of chlorine (by chloride chemical analyses) or 1.0% by weight of Portland cement. Two samples of a mass similar to the premixed samples were wetted as above and tested for chloride. The NMR signal was acquired using a magnetic field strength (B_0) of 2.35 T, a coil diameter (d_{coil}) of 1.5 cm, and a height (h_{coil}) of 3.5 cm. A chloride signal of SNR = 5.9 was detected from the sidewalk sample SW-2 as shown in Table 5 after 262,064 averages taken over 39 h. The FID and the frequency spectrum appear in Fig. 9a and b, respectively.

4. Discussion

4.1. Interpretation of experimental results

The experiments on aqueous solutions demonstrated that chloride was detectable in the 2.35 T magnet used for these experiments. An SNR of 18 was obtained at the most dilute concentrations used in the experiments after a modest

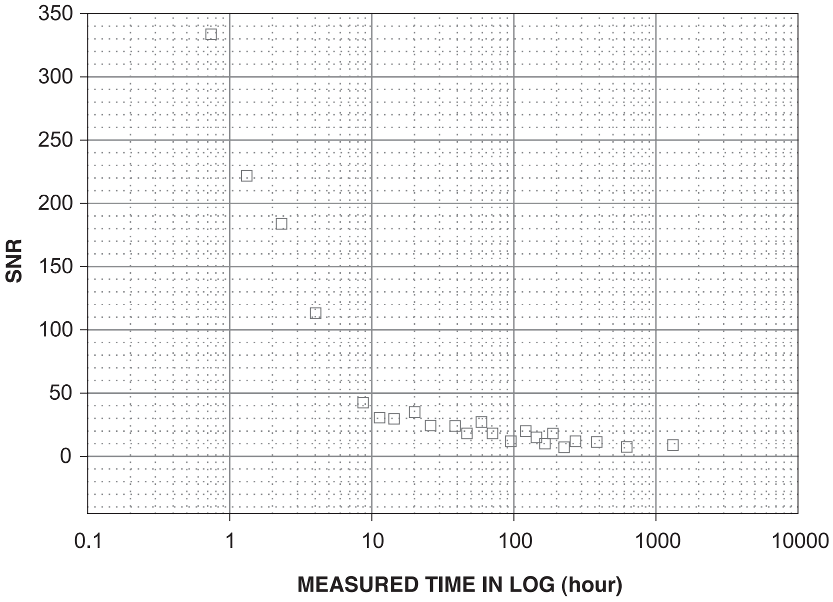


Fig. 7. The decay of the SNR of the cement/sand/NaCl/water sample. The detection of chloride was possible out to over 100 h by use of increased averaging.

Table 4b
SNR determined after oven drying and rewetting sample WPM-2

Sample phase	Weight (g)	Δ weight (g)[a]	Water content (%)[b]	SNR
After curing for 26 days[c]	5.30	–	11.58	7.4
After oven drying for 3 days[d]	4.75	– 0.55	0	[e]
After rewetting for 24 h	4.87	– 0.43	2.53	[e]
After rewetting for another 5 days	4.98	– 0.32	4.84	5.6
After rewetting for another 7 days	5.08	– 0.22	6.95	7.4

[a] Weight change compared to the original sample weight of 5.30 g.
[b] Water content compared to the dried sample weight of 4.75 g.
[c] Sample had been sealed with a plastic cap to avoid loss of water.
[d] Sample was rewetted in a humid chamber to avoid loss of chloride.
[e] No signal was received.

amount of averaging (1024 signals). The measured relaxation times agreed with the values found by Yu and Kirkpatrick [6], where the results overlapped (see Fig. 3). Under optimal conditions for measurement of the chloride NMR signal, a relaxation time of tens of milliseconds was found.

As a check on the internal consistency of the results, we calculated a quantity S_0 that should be proportional to the number of detectable spins. S_0 is defined by Eq. (2).

$$S_0 \equiv \beta v_s M_0 = \frac{\langle S_0 T_2^* \rangle}{T_2^*} \tag{2}$$

where β is a constant that is a function of the apparatus, v_s is the sample volume, and M_0 is the magnetization per unit volume that is proportional to the number of spins present in the sample [12]. The quantity $\langle S_0 T_2^* \rangle$ is the peak value of the Fourier transform of the FID when that decay is a pure exponential. The values of S_0 obtained from the experiments on aqueous solutions of sodium chloride, under the assumption of an exponential FID, appear in Table 1 and are plotted in Fig. 2. Consistent with the theory of NMR, the values of S_0 are approximately proportional to the concentration of chloride atoms in the sample when the sample volume was constant.

The experiments on premixed cement samples showed that the SNR and the apparent relaxation time strongly decreased in the presence of cement (Figs. 5 and 6 and Tables 2 and 3). When the concrete sets and the mobility of the chlorine ion is reduced, other atoms in the concrete interact more strongly with it because chloride, having a quadripolar moment, is influenced by the local electric field. In the liquid state, the chloride atom moves so quickly that the electric field around it changes rapidly and averages to zero. At 10 MHz, where the period is 0.1 μs and where the NMR occurs for chloride at 2.35 T, the averaging rate is very good and the decay time is relatively long, ≈ 20 ms. For chloride in concrete, however, the correlation times of atomic motion in the solid are much longer. The atom spends much more time in the states available to it; hence, relaxation is much more efficient and the decay time is much shorter, approximately 1 ms, to the point where the decay time is roughly equivalent to the interval of ringing in the electronics after the excitation is stopped.

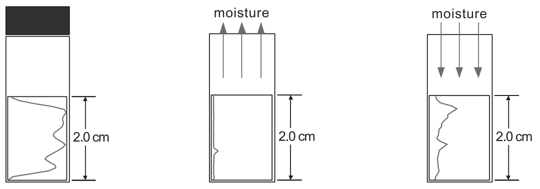
When the measurement delay due to ringdown of the electronics is comparable to the apparent spin–spin relaxation time, T_2^*, the peak of the Fourier transform does not correspond to the signal that would have been detected if the delay had been absent; still assuming an exponentially decaying FID, one nevertheless can correct the peak value for the delay according to Eq. (3).

$$S_0 = \frac{\lim_{\omega \to 0} \int_{t_0}^{\infty} S_{0,\mathrm{app}} \mathrm{e}^{-t/T_2^*} \mathrm{e}^{-j\omega t} \mathrm{d}t}{T_2^* \mathrm{e}^{-t_0/T_2^*}} \tag{3}$$

where $S_{0,\mathrm{app}}\mathrm{e}^{-t/T_2^*}$ is the measured FID and t_0 is the delay time. The quantity S_0 appears in Tables 2 and 3 for the WPC and GPC, respectively. Comparing the values of S_0 found at 3 h after mixing, one finds that they follow the trend of Table 1 where an increased initial chloride concentration corresponds to an increasing value of S_0. Scatter in the data at the lowest initial concentrations is apparent because the relaxation times were almost equal to the delay time, but the overall conclusion is clear that the NMR signal in the presence of cement, at least initially, reflects the amount of chloride added. Furthermore, the magnitudes of S_0 found at 3 h into the experiment are comparable to the values of S_0 detected in the aqueous solutions of Table 1. Clearly, the signal measured from the samples at 3 h reflects the presence of all or at least most of the spins. As time elapses, one no longer detects signal from the more dilute cement samples using only 1024 averages. A precipitous drop (factor of 3) in S_0 occurs in the 0.4%, 1%, and 2% samples between 6 and 12 h into the experiment. Some of the chloride ion must be immobilized in the matrix during this time.

The results in the GPC follow the results for WPC qualitatively. The main differences between the two cases are that the onset of the precipitous decline in S_0 is delayed to occur between 12 and 24 h and the relaxation times are all less than a millisecond.

The two experiments with wetting of concrete samples indicate both that chloride can be detected in concrete when



(a) cured for 26 day after mixing sample (b) oven-dried for 3 days (c) rewetted for 6 days

Fig. 8. One-dimensional proton image for the moisture distribution in the WPC mortar sample with NaCl admixture. (a) Water NMR image after 26 days of curing. (b) Same image after oven drying. (c) Proton image after rewetting.

Table 5
SNR of samples taken from damaged pavement

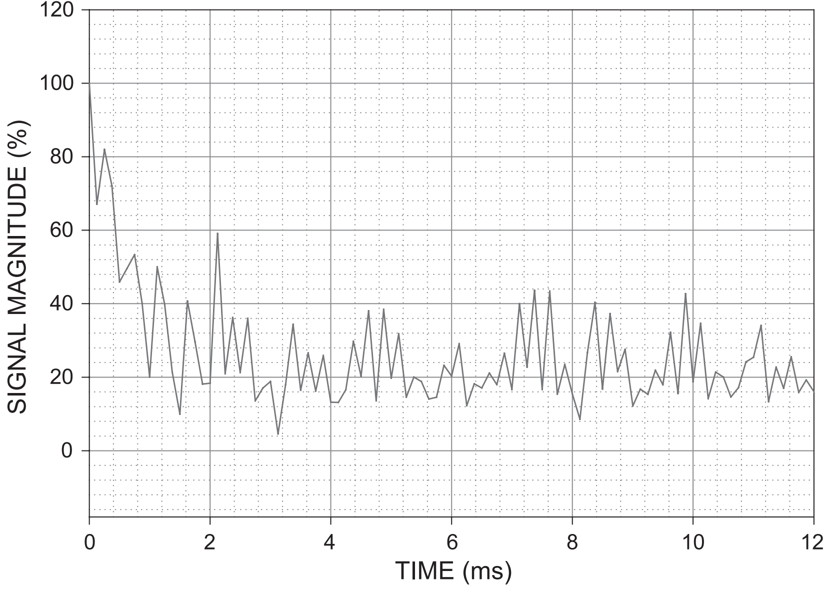
	Weight (g)	Cl by weight of sample (%)	Cl by weight Portland cement (%)	Estimated chlorine weight (g)	Soaked sample weight (g)	Δ weight (g)	Soaking time (h)	Receiver gain	Sampling time (h)	SNR
SW-1	5.31	0.227	1.75	0.012	5.47	0.17 (3.1%)[a]	1	1000	19.5 (131,032 readings)	[b]
SW-2	5.39	0.13	1.0	0.007	5.68	0.21 (3.7%)[a]	5	10,000	39 (262,064 readings)	5.9

[a] Percentage by weight of soaked sample.

[b] No signal was received.

water is present but that the signal is quite weak. The mortar sample, where the chloride was premixed into the cement, provided evidence that the chloride giving a signal was associated with water. A signal from chloride in the cement could be extinguished and then restored by desiccation and rewetting. The chloride measured after rewetting corre-

(a) Free induction decay



(b) Frequency spectrum

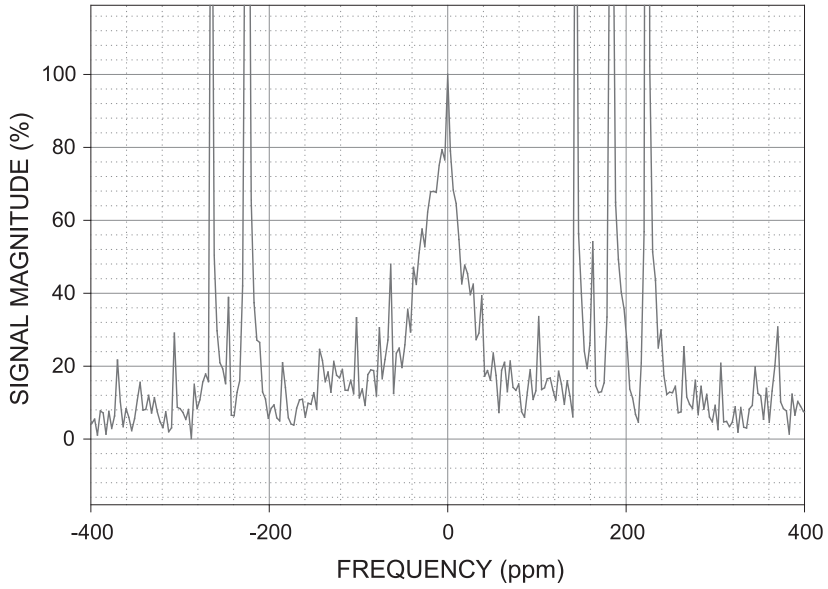


Fig. 9. FID and Fourier transform of the signal from chloride in a wetted field sample (SW-2). Chloride was detected by NMR in this sample.

sponds to free chloride in the concrete that is available for solvation by water and is mobile. This chloride is difficult to measure even in the premixed case because the mobility of the chloride in the pores of the cement is so small. The experiment with a sample of concrete that had been in the field for 20 years showed that a chloride signal could be detected in old concrete when rewetted. The signal in this case required over 200,000 averages to be detected, however.

4.2. Parametric studies of coil dimensions and magnetic field strengths

The SNR is widely accepted as a standard measure to determine the performance of an NMR spectrometer [8]. Hoult and Richards [13] derived an equation (Eq. (4)) of SNR for an NMR system,

$$\mathrm{SNR} = \frac{k_0(B_1/i)\gamma\omega_0^2 v_\mathrm{s} N\hbar^2 I(I+1)/3\sqrt{2}k_\mathrm{B}T}{V_\mathrm{noise}} = \frac{V_\mathrm{signal}}{V_\mathrm{noise}} \tag{4}$$

where k_0 is a scaling constant to account for B_1 inhomogeneity, B_1 is the magnitude of the transverse magnetic field, i is the unit current, γ is the gyromagnetic ratio, ω_0 is the nuclear precession frequency (or Larmor frequency), v_s is the sample volume, N is the spin density, I is the spin quantum number, k_B is the Boltzmann's constant; $\hbar$ is $h/2\pi$, where h is Planck's constant, T is the sample absolute temperature, and V_noise is the noise in volts.

Peck et al. [8] derived the relationship (Eq. (5)) of the SNR per unit volume ($\mathrm{SNR}_\mathrm{puv}$) for a solenoid-shaped coil taking into account conductive and dielectric losses,

$$\mathrm{SNR}_\mathrm{puv} \propto \frac{\omega_0^2\left[\dfrac{n}{d_\mathrm{coil}\sqrt{1+(h_\mathrm{coil}/d_\mathrm{coil})^2}}\right]}{\sqrt{n^2 d_\mathrm{coil}\omega_0^{1/2}/h_\mathrm{coil}}} = \sqrt{\frac{a}{1+a}}\frac{\omega_0^{7/4}}{d_\mathrm{coil}} \propto \frac{\omega_0^{7/4}}{d_\mathrm{coil}} \tag{5}$$

where $a = h_\mathrm{coil}/d_\mathrm{coil}$ is constant and n is the number of turns of the coil.

If we assume that the sample volume is linearly proportional to coil size, the SNR can be obtained from Eq. (6),

$$\mathrm{SNR} \propto \sqrt{\frac{a}{1+a}}\frac{\omega_0^{7/4}}{d_\mathrm{coil}}v_\mathrm{s} \propto \sqrt{\frac{a^3}{1+a}}\omega_0^{7/4}d_\mathrm{coil}^2 \propto \omega_0^{7/4}d_\mathrm{coil}^2 \tag{6}$$

where h_sample is the sample height ($\propto h_\mathrm{coil}$) and d_sample is the sample diameter ($\propto d_\mathrm{coil}$).

If we assume further that all of the parameters are the same except sample volume (v_s), transverse magnetic field strength (B_1/i) due to coil size (d_coil and h_coil), longitudinal magnetic field strength (B_0) and noise (V_noise) due to resistance of coil (R_coil), and that ω_0 is linearly proportional to the magnitude of the longitudinal magnetic field (B_0) ($\omega_0 = \gamma B_0$), we can estimate the SNR of a solenoid coil with different coil diameters and Larmor frequencies as shown in Eq. (7).

$$\mathrm{SNR}[\mathrm{designed}] = \left(\frac{B_0[\mathrm{designed}]}{B_0[\mathrm{measured}]}\right)^{7/4} \times \left(\frac{d_\mathrm{coil}[\mathrm{designed}]}{d_\mathrm{coil}[\mathrm{measured}]}\right)^2 \mathrm{SNR}[\mathrm{measured}] \tag{7}$$

Having a signal from the rewetted sidewalk sample SW-2 as per Fig. 9, we performed a parametric study using Eq. (7), the SNR for the sample SW-2, and an assumption that all test parameters are the same test parameters except for the sample size (v_s), transverse magnetic field strength (B_1/i), longitudinal magnetic field strength (B_0), and resistance of the coil (R_coil). The SNR of a signal averaged over N readings, $\mathrm{SNR}_{(N)}$, was estimated to be the square root of the number of readings, N, times the SNR of a signal from only one reading, $\mathrm{SNR}_{(1)}$. A minimum measurement time of 3 h and a maximum measurement time of 24 h were assumed for this parametric study. The chlorine concentration of the sample for these estimations was taken to be 0.1% by weight of Portland cement, a value 50% below the threshold content of acid-soluble chloride necessary to initiate corrosion of reinforcement steel [1].

Table 6a gives the estimated SNR values for different coil diameters (10–70 mm) and magnetic field strengths (0.5–20 T) when averaging over 19,654 readings, which takes about 3 h. Table 6b gives the estimated SNR values for different coil diameters (10–70 mm) and magnetic field strengths (0.5–20 T) averaged over 161,270 readings (about 24 h). From Tables 6a and 6b, the SNR values of the proposed in situ NMR sensor described in Section 1.2, with a longitudinal magnetic field strength (B_0) of 0.5 T and a coil diameter (d_coil) of 2–4 mm, are estimated to be less than 0.0049 and 0.014 for 3 and 24 h worth of signal averaging, respectively. Thus, the embedded NMR concept described in Section 1.2 is not feasible to detect a chlorine signal from mature concrete containing a chloride ion concentration of 0.1% by weight of Portland cement. However, also based on Tables 6a and 6b, it must be noted that at magnetic field strengths around 2–3 T and at coil diameters around 50–70 mm, SNR values around 5 can be achieved even for the minimum amount of sampling time considered in this study (3 h).

4.3. Implications of the parametric studies

For the proposed in situ NMR sensor to be embedded into concrete, the sensor size should be smaller than the depth of concrete cover. A typical depth of concrete cover for protecting reinforcement steel against corrosion is 3/8–3 in. (or 9.5–76.2 mm) [14]. If we assume that the maximum

Table 6a
Estimated SNR values for in situ sensor with varying coil diameters, magnetic field strengths, and number of signals averaged

Coil diameter (mm)	Magnetic Field Strength, B_0 (T)									
	0.5 T	1.0 T	1.5 T	2.0 T	2.35 T	3.0 T	5.0 T	10 T	15 T	20 T
(a) SNR values when averaging over 19,654 readings (equivalent sampling time of 3 hours)										
10	4.9e-3	1.6e-2	3.3e-2	0.1	0.1	0.1	0.3	0.9	1.9	3.1
20	2.0e-2	0.1	0.1	0.2	0.3	0.5	1.1	3.7	7.5	12.5
30	4.4e-2	0.1	0.3	0.5	0.7	1.0	2.5	8.3	16.9	28.0
40	0.1	0.3	0.5	0.9	1.2	1.8	4.4	14.8	30.1	49.8
50	0.1	0.4	0.8	1.4	1.8	2.8	6.9	23.1	47.0	77.8
60	0.2	0.6	1.2	2.0	2.6	4.1	9.9	33.3	67.8	112.1
70	0.2	0.8	1.6	2.7	3.6	5.5	13.5	45.4	92.2	152.6
(b) SNR values when averaging over 161,270 readings (equivalent sampling time of 24 hours)										
10	1.4e-2	4.6e-2	0.1	0.2	0.2	0.3	0.8	2.6	5.2	8.7
20	0.1	0.2	0.4	0.6	0.8	1.3	3.1	10.3	21.0	34.7
30	0.1	0.4	0.8	1.4	1.8	2.8	6.9	23.2	47.2	78.1
40	0.2	0.7	1.5	2.5	3.3	5.0	12.3	41.3	83.9	138.8
50	0.3	1.1	2.3	3.9	5.1	7.8	19.2	64.5	131.1	216.8
60	0.5	1.7	3.4	5.6	7.4	11.3	27.6	92.8	188.7	312.2
70	0.7	2.2	4.6	7.6	10.0	15.4	37.6	126.4	256.9	425.0

Notes:

- To estimate the SNR, the SNR of 5.9 for damaged pavement sample DP-2 was used.
- The sample contains chlorine of 0.007 g or 1.0% by weight of Portland cement.
- To account detection limit of 0.1% chlorine concentration, the SNR for the pavement sample was multiplied by a factor of 0.1 before being used in Eq. (6).
- The magnetic field strength (B_0) = 2.35 T.
- The coil diameter (d_{coil}) = 1.5 cm and the coil height (h_{coil}) = 3.5 cm.
- The number of readings averaged in the pavement sample experiment is 262,064 readings (equivalent sampling time: 39 h).
- Grayed-out cells are for the configurations where the SNR is greater than 5.

sensor size is 70% of the concrete cover depth, when the concrete cover depth is 70 mm, the maximum sensor size will be 50 mm on a side. If we consider the volume of a permanent magnet, electronics, and sensor package, the coil diameter and hence the maximum sample diameter will be less than 5 mm. There is no magnetic field strength on Table 6a that produces an SNR greater than 5 after 20,000 detection cycles and only a field greater than 15 T produces an SNR greater than 5 in a sample dimension twice the expected maximum after 160,000 readings. The clear conclusion is that detection of chloride in small volumes of cement is not practical and hence the concept of an embedded system based on NMR for chloride detection is probably not feasible.

If one cannot embed an entire system, it would be necessary to deliver a homogeneous magnetic field from above the surface of the concrete. This is the concept sometimes known as the inside-out NMR. The remote production of a homogeneous magnetic field was reported by researchers at the Los Alamos Scientific Laboratory [15–17]. Their approach involved two aligned equal magnetic field sources separated by a certain distance. When the same polarities of these two fields oppose each other, a toroidal region of homogeneous magnetic field is generated. The location of this toroidal region can be adjusted by changing the separation between two magnets. The field strength of the toroidal region is proportional to the strength of the two magnets. In the experiment by Jackson et al. [17], they detected a proton signal from the sample placed in a toroidal region of the remote magnetic field that was separated by 14 cm from the axis of the two magnets. The magnetic field strength of the toroidal region was 0.012 T in their experiment. This small field underscores the difficulty of trying to increase sample volume by going to external magnetic field generation. A magnetic field strength of 10^{-2} T makes any attempt to detect chloride problematic. The only way around these fundamental problems is to find a way to increase the homogeneous magnetic field strength cast from an external magnet and to concentrate the chloride at a detection node buried in the concrete.

5. Summary

The feasibility of using an embedded NMR device to determine chloride levels in concrete structures and record the changes in chloride levels and profiles with depth was investigated and discussed in this paper. The intrusion of chloride ions from deicing agents into concrete, and the resulting corrosion of embedded steel reinforcement, is the major cause of infrastructure (bridges, roads, parking structures, etc.) deterioration in this country. Chlorine signals were detected with a 2.35-T NMR spectrometer from samples of cured WPC mixed with NaCl, GPC samples mixed with NaCl and a sample taken from damage sidewalks. Residual free chloride was detectable in the cement using NMR. Using the measured chlorine signal from a sample taken from a field sample, a parametric study was performed with various values for the magnetic field strength, coil diameter, and measurement time to estimate the signal-to-noise (SNR) ratio of a proposed in situ NMR sensor that would use a 0.5 T magnetic field and a 2- to 4-mm diameter microcoil. According to this parametric study, the SNR of the envisioned in situ NMR sensor averaged for 24 h with a longitudinal magnetic field of 0.5 T and coil diameter of 2–4 mm would be far below 1. However, at magnetic field strengths around 2–3 T and at coil diameters around 50–70 mm, it is estimated that SNR values around 5 can be achieved even for the minimum amount of sampling time considered in this study (3 h). The problem is that homogeneous field strengths of this size would be difficult to produce at remote sites. The challenge would be to somehow concentrate the chloride and average for a long enough time to extract a signal.

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