

New insights into autogenous self-healing with NMR tests

Huang H.^{1,2*}, Ye G.^{2,3} and Pel L.⁴

1. School of Materials Science and Engineering, Southeast University, Nanjing 211189, China

2. Faculty of Civil Engineering and Geosciense, Delft University of Technology, Delft 2628CN, the Netherlands

3. Department of Structural Engineering, Ghent University, Ghent 9052, Belgium

4. Department of Applied Physics, Eindhoven University of Technology, Eindhoven 5600 MB, the Netherlands

Abstract

Concrete is a brittle composite cementitious material that easily fractures under tensile loading. Microcracks can appear throughout the concrete prior to application of any load because of temperature-induced strain and autogenous and drying shrinkage. There is no doubt that these cracks provide preferential access for aggressive agents to penetrate into the concrete, probably causing corrosion of reinforcement steel and degradation of concrete. As a result, the service life of reinforced concrete structures is shortened. Fortunately, concrete has the ability to heal the crack itself without manual efforts when water is present in cracks. This ability is defined as autogenous self-healing. However, the effect of migration of water from cracks into the bulk paste on autogenous self-healing is not clear yet.

The aim of this study is to investigate the effect of water migration from cracks into the bulk paste on autogenous self-healing. Nuclear magnetic resonance (NMR) technique was utilized to monitor water migration from cracks into the bulk paste during the process of autogenous self-healing. NMR results show that in the beginning of autogenous self-healing the water in the crack migrates into the bulk paste and the water content of the bulk paste increases significantly. However, after 5-hour autogenous self-healing period the amount of non-chemically bound water in the bulk paste (adjacent to the crack surfaces) determined by NMR decreases instead. It indicates that some of the water coming from the crack was used by additional hydration of unhydrated cement particles in the bulk paste during the process of autogenous self-healing. NMR results reflect that most of the reaction products of additional hydration are formed in the bulk paste adjacent to the crack surfaces, rather than in the crack. Because of the additional hydration caused by the water from the crack, the capillary porosity of the bulk paste adjacent to the crack surfaces decreases significantly.

Before this work the filling of cracks is the main concern in term of autogenous self-healing. The densification of the cement paste adjacent to the crack surfaces, which was observed for the first time in this study, will also decrease the ingress of aggressive agents into the bulk concrete matrix and prolong the service life of concrete structures. This observation provides a new insight into autogenous self-healing in cement paste.

Originality

In this study, the effect of migration of water from cracks into the bulk paste on autogenous self-healing was investigated by means of NMR technique for the first time. NMR results show that some of the water coming from the crack was used by additional hydration of unhydrated cement particles in the bulk paste during the process of autogenous self-healing. The microstructure of the bulk paste adjacent to the crack surfaces, therefore, becomes much denser than in the paste where water from the cracks can not reach. Before this work the filling of cracks is the main concern in term of autogenous self-healing. The densification of the cement paste adjacent to the crack surfaces, which was observed for the first time in this study, will also decrease the ingress of aggressive agents into the bulk concrete matrix and prolong the service life of concrete structures. This observation provides a new insight into autogenous self-healing in cement paste.

Keywords: autogenous self-healing, water migration, additional hydration, densification of microstructure, nuclear magnetic resonance (NMR)

¹ Corresponding author: h.l.huang@msn.com

1. Introduction

Usually, concrete is designed to crack to make the steel reinforcement adequately carry tensile loads (van Breugel, 2012). Moreover, microcracks can appear throughout the concrete prior to application of any load because of temperature-induced strain and autogenous and drying shrinkage (van Breugel, 2012). There is no doubt that these cracks provide preferential access for aggressive agents to penetrate into the concrete, probably causing corrosion of reinforcement steel and degradation of concrete. As a result, the service life of reinforced concrete structures is shortened.

According to Hearn (1998), by the end of nineteenth century it had already been noticed that cracks in water retaining structures, culverts and pipes were gradually filled without any artificial efforts. The filling of cracks with reaction products decreases permeability of concrete (Clear, 1985) and the ingress of chloride ions (Fidjestol and Nilsen, 1980). The filling of cracks without any artificial efforts was defined as autogenous healing of concrete (Soroker and Denson, 1926). It has been recognized that water is essential for autogenous self-healing (Hearn, 1992). On the one hand water in cracks serves as a reactant and on the other hand as a medium in which ions can transport and reaction products can precipitate. It is conceivable that if cement paste is not saturated with water, in the healing process the water in the crack can migrate into the bulk paste. However, by now the effect of migration of water from cracks into the bulk paste on autogenous self-healing is still not clear yet.

In this study, nuclear magnetic resonance (NMR) technique was utilized to investigate water migration from cracks into the bulk paste during the process of autogenous self-healing. The changes of water content and water distribution in the bulk paste adjacent to the crack surfaces were quantified by NMR. The effect of migration of water from cracks into the bulk paste on autogenous self-healing was analyzed.

2. Material and specimen preparation

2.1 Material

The material used in this study was Portland cement paste made of CEM I 42.5N. The chemical composite of Portland cement CEM I 42.5N is shown in Table 1. The water to cement ratio (w/c) of the cement paste was 0.3.

Table 1: Chemical composites of Portland cement (CEM I 42.5N)

Compound	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	SO ₃	MgO	Total
Weight (%)	64.40	20.36	4.96	3.17	0.64	0.14	2.57	2.09	98.33

2.2 Specimens prepared for NMR tests

In this study, prism specimens with a dimension of 20 mm × 20 mm × 145 mm were cast. After casting, the specimen was cured under sealed conditions. A glass tube with an outside diameter of 4 mm and a wall thickness of 0.7 mm was embedded inside the specimen for delivering extra water (i.e. the water supplied to the sample after cracking) to the crack for autogenous self-healing.

At the age of 40 days, the specimen was split into two pieces (see Figure 1). The two pieces of the broken specimen were pressed together from both ends in axial direction and glued at the outside with a high viscosity epoxy. Moreover, the surfaces of the cracked specimens were sealed with the same epoxy except both end surfaces (see Figure 1). The viscosity of the epoxy was high enough to ensure that the epoxy did not penetrate into the crack (For the tests in this chapter, some specimens were cut and checked to make sure that no epoxy had penetrated into the crack). After the epoxy got hardened, the specimen was ready for the tests.

At the age of 42 days, extra water was delivered to the crack via the glass tube. When the glass tube was filled with water, the water in the glass tube easily penetrated into the crack and induced autogenous self-healing.

3. NMR experiment

3.1 NMR setup

In this study, a NMR setup was used which is especially designed for quantitative moisture measurements in building materials (see Figure 2). This NMR setup was operated at a main field of 0.8 Tesla. A Faraday shield was placed between the radio frequency (RF) coil and the sample holder.

The use of Faraday shield was to suppress the effects of the changes of the dielectric permittivity by variations of the water content, thereby making the NMR measurements quantitative (Kopinga and Pel, 1994, Pel, 1995). In order to measure a moisture profile the sample can be moved through the NMR with the help of a stepper motor. In this study we have used a step size of 2.5 mm.

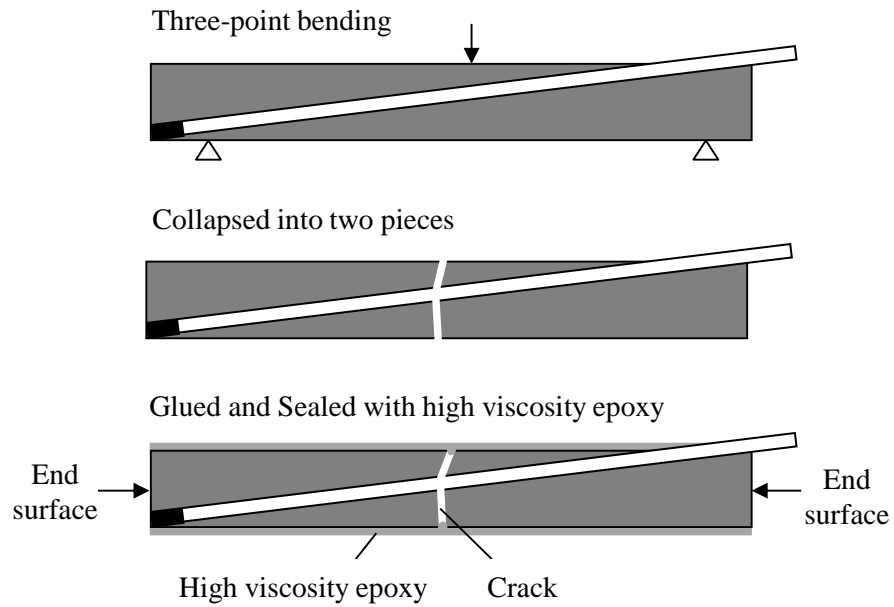


Figure 1 A schematic diagram of the specimen for the NMR experiment.

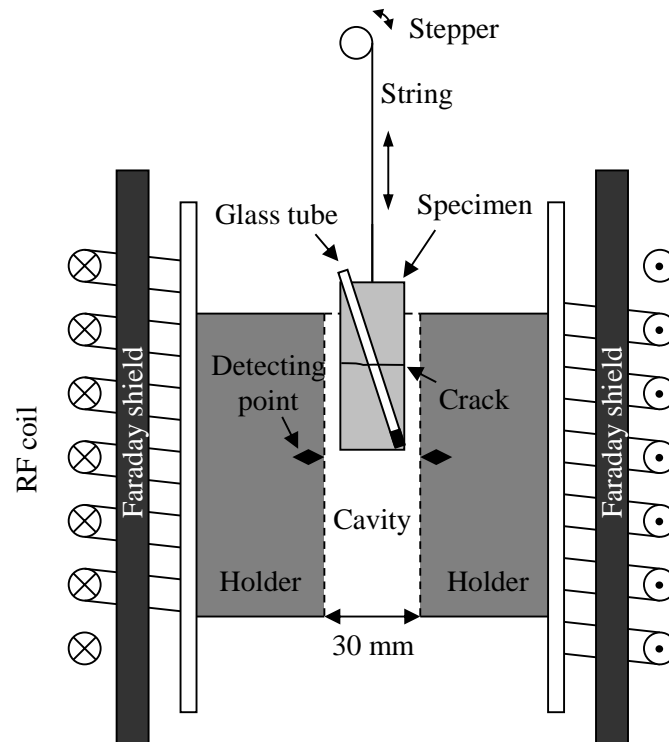


Figure 2 A schematic diagram of NMR setup.

3.2 Calibration

In order to quantify the amount of non-chemically bound water in the sample, the NMR signal against the water content of the sample was calibrated. The initial weight of a specimen at the age of 42 days was measured first. The signal of the water profile of the specimen was measured by NMR as well. After that, the specimen was submersed in water. After absorbing water for a certain time, the sample was weighed again. The signal of water profile of the specimen was immediately measured as well. All the measurements of the water profile were carried out with the same settings of the NMR equipment. In this study, the calibration was done within a short period (i.e. less than 2 hours).

It is known that the increase of the NMR signal must be linear to the amount of absorbed water (Valckenborg et al., 2001). As shown in Figure 3, in this experiment the increase of NMR signal of the specimen was linear to the amount of water absorbed by the specimen, indicating the NMR machine used in this study can quantify the amount of non-chemically bound water accurately.

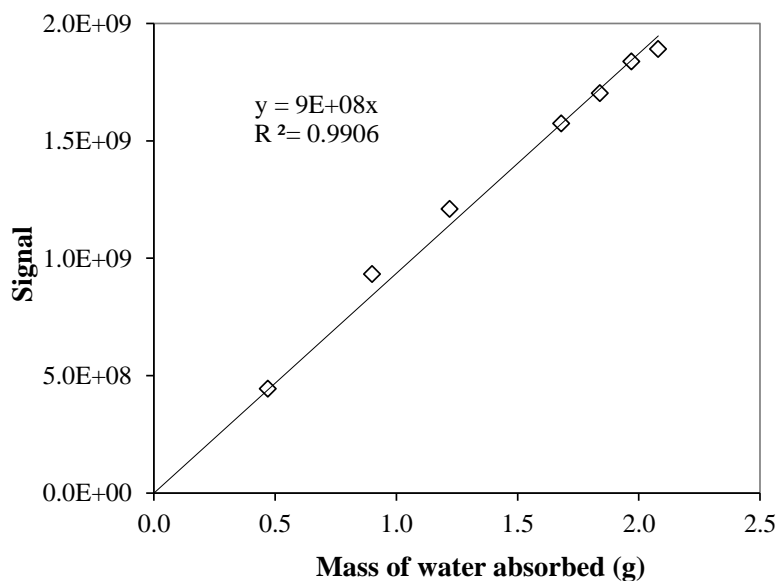
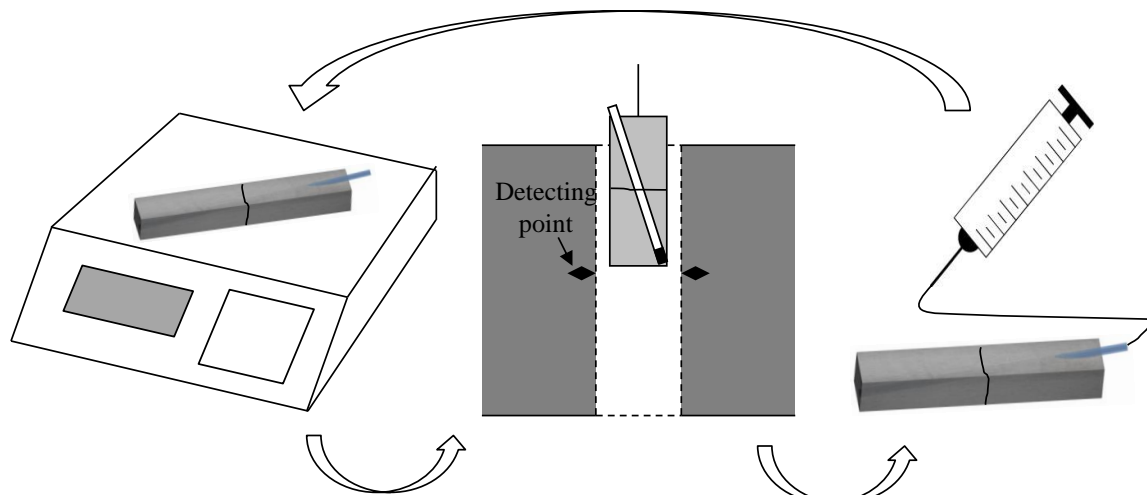


Figure 3 Relationship between NMR signal and the mass of water absorbed by the sample

3.3 Test procedures

After calibration, migration of extra water from the crack into the bulk cement paste during the process of autogenous self-healing can be monitored by NMR tests.

As illustrated in Figure 4, at the start of the experiment the initial mass of the specimen was weighed. The specimen was then placed to the NMR equipment and its initial water profile was measured. Then the specimen was taken away from the NMR equipment and the glass tube of the specimen was filled with water by using a syringe. When the glass tube was filled, the specimen was weighed again. After that the specimen was placed back to the NMR equipment for measuring the water profile again. By repeating these procedures, i.e., filling the glass tube, weighing the specimen and measuring the water profile, the amount of water absorbed by the bulk cement paste as a function of time was determined. The change of the distribution of water within the specimen was monitored.



Step I: Weighing the mass of the specimen

Step II: Measure the water profile of the specimen with NMR

Step III: Glass tube in the specimen filled with water

Figure 4 A flow diagram of the experimental procedure

4 Experimental results and discussion

4.1 Water migration from the crack into bulk paste

Figure 5 shows the NMR signal profiles of the specimen at different period of autogenous self-healing (from 5.0 h to 22.0 h). From the signal profile for $t=0$ h (before the injection of water), it is found that water is distributed uniformly inside the specimen. As can be seen from the profile for $t=0.7$ h, after water was injected into the glass tube, a sharp peak occurred at the position of the crack about 66 mm from the bottom of the specimen (the position of 0 corresponds to the bottom of specimen). It indicates that the injected water has penetrated into the crack and has started to migrate into the bulk paste. With increase of time, the intensity of the peak increased and the sharp fronts of the peak moved toward both ends of the specimen. It demonstrates that water migrated into the bulk paste from the crack and the water content of the cement paste nearby the crack increased significantly. After the glass tube had been fully filled with water for 5.0 hours, the peak of the water profile measured in the region near the crack did not increase any more (compare the water profile at 5.0 h with that at 22.0 h in Figure 5).

4.2 Autogenous self-healing – *Densification of the bulk paste adjacent to the crack surfaces*

Figure 6 shows that the fronts of water profile hardly move after 22-hour exposure of the crack to water for autogenous self-healing. Moreover, the peak of the water profile decreases with increase of time, which is different from that before 22 hours (the peak of water profile increases before 22 hours, as shown in Figure 5). It should be mentioned that the glass tube remained filled with water during the test. It is not conceivable that there was a lack of water supply.

Note that in this experiment cement paste with a low w/c ratio of 0.3 was used. The degree of hydration of cement prior to the start of the tests is about 70% at the age of 42 days according to the modeling by using HYMOSTRUC3D (van Breugel, 1991, Koenders, 1997, Ye, 2003). Hence, there was still unhydrated cement left in the bulk paste due to the lack of water (Powers, 1948). The extra water supplied via the tube promoted further hydration of the unhydrated cement particles in the bulk paste adjacent to the crack surfaces (as illustrated in Figure 7).

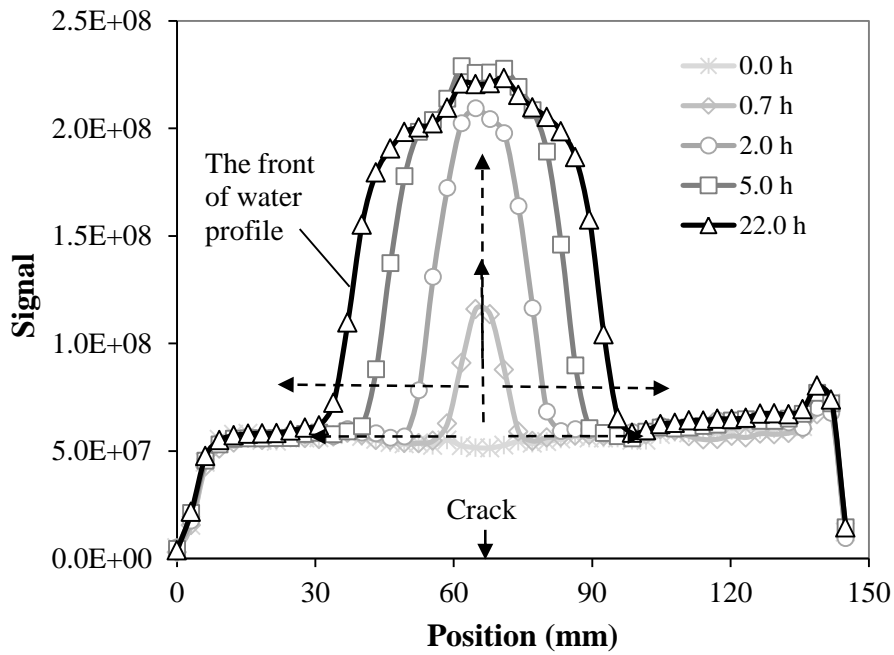


Figure 5 NMR signal profiles after the supply of extra water for autogenous self-healing for different time until 22 hours. The cracked specimen is made of cement paste with w/c ratio of 0.3. The supply of water starts at the age of 42 days of the specimen.

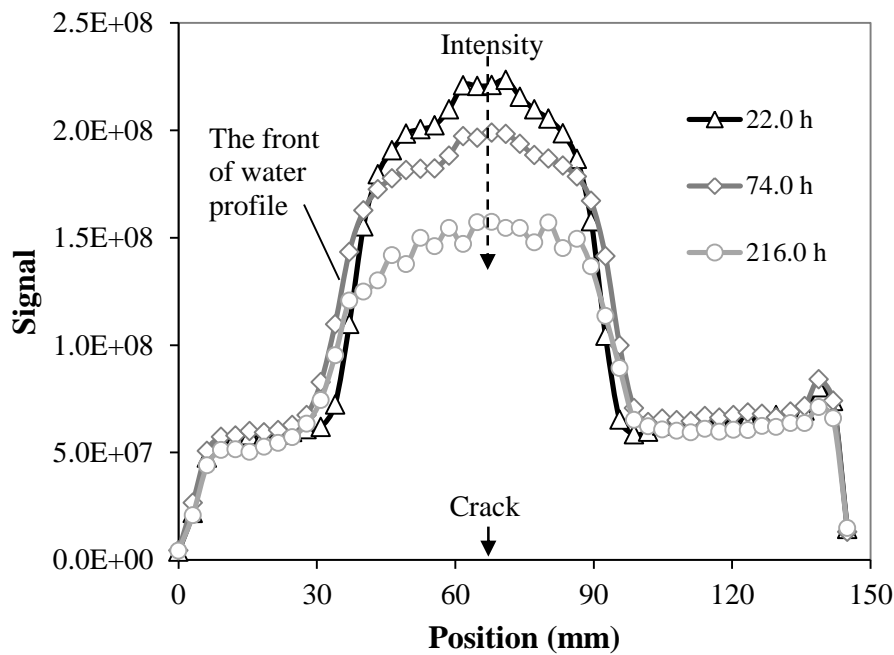


Figure 6 NMR signal profiles after the supply of extra water (from 22 hours to 216 hours) for autogenous self-healing. The specimen is made of cement paste with w/c ratio is 0.3. The supply of water starts at the age of 42 days of the specimen.

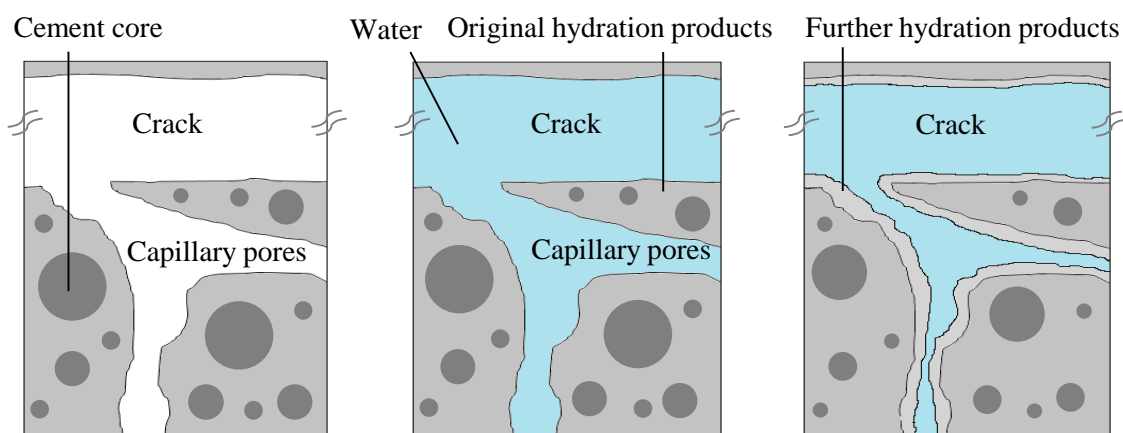


Figure 7 Scheme of further hydration of unhydrated cement (in the cement paste adjacent to the crack surfaces) promoted by extra water coming from the crack in the process of autogenous self-healing

4.3 Quantification of the extra water used by additional hydration of unhydrated cement

Figure 8 shows the amount of absorbed water measured with balances, compared with the extra water measured by NMR. In the beginning of the test (until $t=5$ hours), the amount of extra water in the specimen measured with balance was almost the same as that measured by NMR. However, after 5-hour exposure of the crack to water for autogenous self-healing, the difference between these two groups of values became noticeable. As discussed in the previous section, further hydration of unhydrated cement particles in the bulk paste adjacent to the crack surfaces can be promoted by extra water coming from the crack. Therefore, a part of this extra water was used for further hydration of unhydrated cement particles in the bulk paste. Because the NMR equipment used in this test can only detect the non-chemically bound water inside the paste, the difference between the amount of absorbed water measured with balances and measured by NMR (see Figure 8) indicates the transformation of non-chemically bound water into chemically bound water as a result of additional hydration in the bulk paste nearby the crack surfaces. Because of additional hydration caused by the water coming from the crack, the capillary porosity of the bulk paste adjacent to the crack surfaces decreases significantly. The densification of the bulk paste adjacent to the crack surfaces can decrease the ingress of harmful ions into concrete matrix and slow down degradation of the concrete.

4.4 Positions of additional hydration products – in the crack or in the capillary pores in the bulk paste?

As demonstrated by Huang et al. (2013), in the process of autogenous self-healing, reaction products are formed in the crack. It is interesting to see how the filling of the crack with reaction products influences the NMR signal. As shown in Figure 9, some sections of the specimen tested by NMR (indicated as measured sections) were intersected by the crack. In the measured sections intersected by the crack, not only the water in bulk paste, but also the water in the crack was measured. As self-healing of the crack proceeded, the space of the crack was filled with reaction products. This filling of the crack can also contribute to the decrease of NMR signal. However, as explained in Figure 9, in this test the distance between each measured section was 2.5 mm. Because the height difference between the highest position of the crack and the lowest position of the crack in the tested specimen was about 4 mm (see Figure 9), there were only one or two measured sections intersected by the crack. It means that the filling of the crack can only affect one or two NMR signal reading. The decrease of NMR signal (in Figure 6) measured in other sections is only due to the formation of hydration products in capillary pores, rather than in the crack.

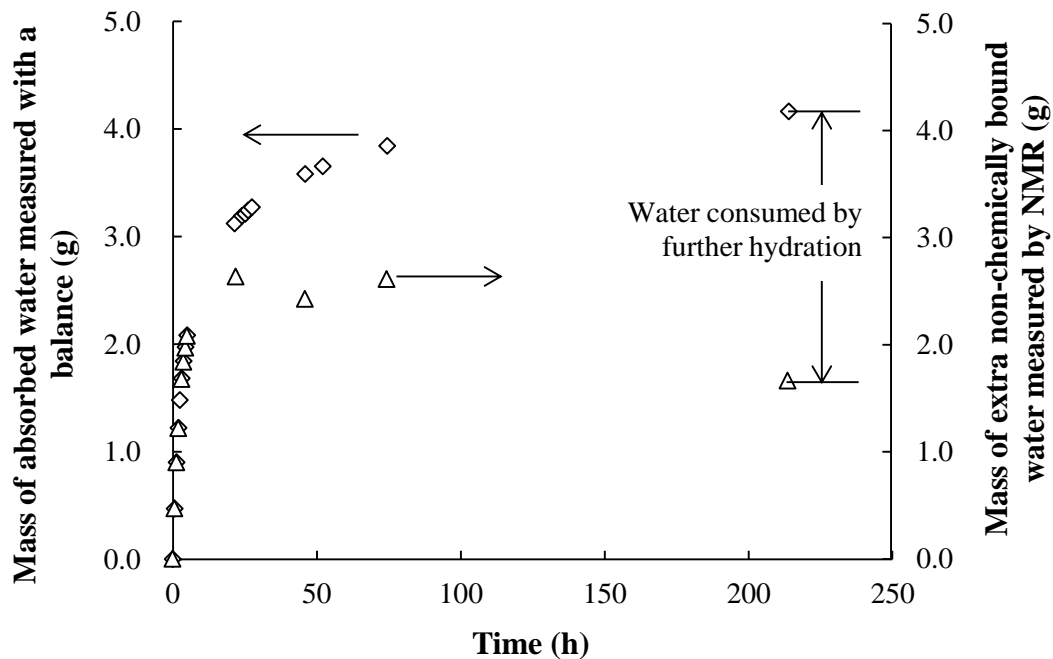


Figure 8 Amount of absorbed water measured by a balance compared with the amount of non-chemically bound water measured by NMR. Time 0 refers to the beginning of the supply of extra water, which is from the age of 42 days of the cement paste.

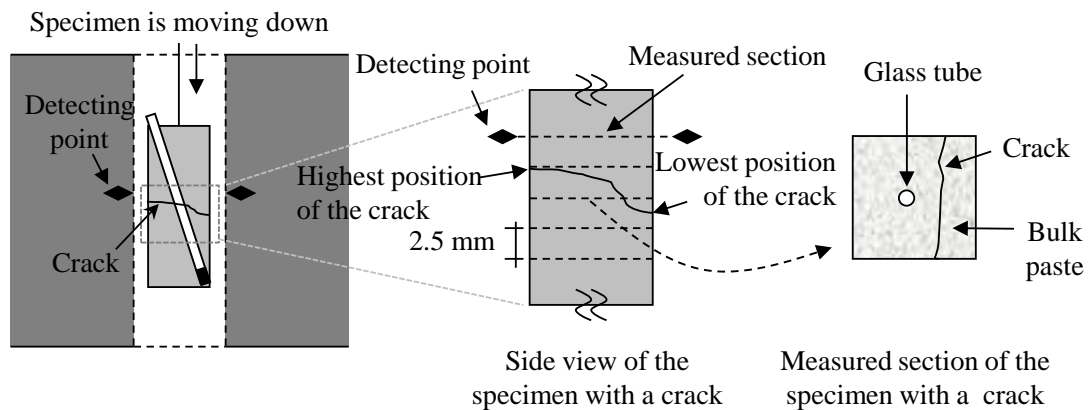


Figure 9 A schematic diagram on the positions of measurements by NMR and the measured sections intersected by the crack

5. Conclusions

Nuclear magnetic resonance (NMR) technique was utilized to investigate water migration from cracks into the bulk paste during the process of autogenous self-healing. The changes of water content and water distribution in the bulk paste adjacent to the crack surfaces were quantified by NMR. From the experimental study, it was noticed that additional hydration taking place in the cement paste adjacent to the crack surfaces during the process of autogenous self-healing. The following conclusions can be drawn:

- When water penetrates into the cement paste (water to cement ratio of 0.3 at the age of 42 days) from a crack, NMR signal for all the pores in the paste adjacent to the crack increases first and then decreases.

- In the beginning of the test, the amount of absorbed water in the specimen measured with balances was almost the same as that measured by NMR. However, after 5-hour exposure of the crack to water, the difference between these two groups of values became noticeable.
- The difference between the amount of extra water measured with balances from that measured by NMR indicates that some of the extra water was used by additional hydration of unhydrated cement particles in the bulk paste.
- NMR results show that the additional hydration products mainly form in the pores in the bulk paste adjacent to the crack surfaces, instead of the crack.

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References

- Clear, C. A. (1985) The effect of autogenous healing upon leakage of water through cracks in concrete. Tech. Report 559.
- Fidjestol, P. and N. Nilsen (1980) Field Test of Reinforcement Corrosion in Concrete. ACI special publications: 205-221.
- Hearn, N. (1992) Saturated permeability of concrete as influenced by cracking and self-sealing. PhD, University of Cambridge.
- Hearn, N. (1998) Self-sealing, autogenous healing and continued hydration: What is the difference? *Materials and Structures* 31(8): 563-567.
- Huang, H., G. Ye and D. Damidot (2013) Characterization and quantification of self-healing behaviors of microcracks due to further hydration in cement paste. *Cement and Concrete Research* 52: 71-81.
- Koenders, E. A. B. (1997) Simulation of Volume Changes in Hardening Cement-based Materials. PhD, Delft University of Technology.
- Kopinga, K. and L. Pel (1994) One - dimensional scanning of moisture in porous materials with NMR. *Review of Scientific Instruments* 65(12): 3673-3681.
- Pel, L. (1995) Moisture transport in porous building materials. Ph.D, Eindhoven University of Technology.
- Powers, T. C. a. B., T.L. (1948) Studies of the physical properties of hardened Portland cement paste (9 parts), *J Amer Concr Inst* 43, Bulletin 22, Chicago.
- Soroker, V. J. and A. J. Denson (1926) Autogenous healing of concrete. *Zement* 25(30).
- Valckenborg, R., L. Pel, K. Hazrati, K. Kopinga and J. Marchand (2001) Pore water distribution in mortar during drying as determined by NMR. *Materials and Structures* 34(10): 599-604.
- van Breugel, K. (1991) Simulation of Hydration and Formation of Structure in Hardening Cement-based Materials. PhD, Delft University of Technology.
- van Breugel, K. (2012). Self-healing material concepts as solution for aging infrastructure. 37th Conference on Our World in Concrete & Structures. Singapore.
- Ye, G. (2003) Experimental Study and Numerical Simulation of the Development of the Microstructure and Permeability of Cementitious Materials. PhD, Delft University of Technology.