Non-destructive Evaluation by Single-Sided Nuclear Magnetic Resonance of the Change of Porosity in Concrete due to Thermal Exposure

Robert SCHULTE HOLTHAUSEN, Oliver WEICHOLD

Abstract: In a joint program, the Institutes of Building Materials Research and Mineral Engineering of the RWTH Aachen University are currently developing a new technology to coat concrete with coherent layers of glass by flame spraying. Results indicate that a major factor influencing the pull-off strength of the glass coating is the thermally induced damage in the underlying concrete substrate. In this proceeding, the authors employ a non-destructive test method using single-sided $^1$H nuclear magnetic resonance (NMR) to evaluate the change in porosity in concrete specimens due to the thermal exposure. This particular NMR device primarily records depth profiles of the water content. In addition the relative size of water-filled voids such as pores and cracks can be assessed. For this, the treated samples are water-saturated before recording. The results are compared with the adhesion strength and microscopic images as well as changes in porosity reported in the literature, showing good accordance.

Keywords: nuclear magnetic resonance, NMR-MOUSE, flame spraying, concrete, thermal spalling, NDT, non-destructive testing

1 Introduction

The Institutes of Building Materials Research (ibac, Prof. Raupach and Prof. Weichold) and Mineral Engineering (GHI, Prof. Conradt) of the RWTH Aachen University are currently developing a new technology for seamless glass coatings made by flame spraying for the protection of concrete surfaces. Major challenges in this project include the improvement of the corrosion resistance of the glass layers, as well as the development of a suitable application process to reduce thermal damage in the concrete surface while at the same time enhancing adhesion and reducing permeability in the sprayed glass [1]. Preliminary results on the influence of heat exposure on concrete specimens measured by single-sided nuclear magnetic resonance were reported in [2].

The alteration of the pore structure in concrete due to high temperature exposure were described by Hinrichsmeier [3]. He was able to show a decrease of gel porosity at around 1 nm pore size in the cement stone, whereas the capillary porosity increased in amount and pore size up to 100 nm. He was able to differentiate between the change in the cement stone and the damage in the interfacial transition zone, causing an increased porosity in a range up to 10 μm and greater.

$^1$H nuclear magnetic resonance (NMR) is a technique, widely used in medicine, chemistry, and geophysics, and it is comparatively new in civil engineering [4]. In its application on porous materials such as concrete, it is widely accepted, that the NMR signal can be correlated to the water content inside the observed volume [4, 5]. The relaxation behaviour of the proton spins provides information about the surrounding pore structure [5]. It is known, that shorter relaxation-times $T_2$ are associated with smaller pore sizes and vice versa. Fischer [6] analysed specimens made from grey cement and reported relaxation times of 0.25 ms, 1.25 ms, and a baseline (indicating long relaxation-times) and attributed these to gel, interhydrate, and void porosity respectively.
2 Experiments

Information on the concrete under investigation, the glass material applied and the application process, shown in Figure 1a), can be taken from [1]. This proceeding reports the results of one sample with a glass coating applied by flame spraying. In general, it is difficult to measure the exact surface temperature of concrete samples while spraying. Visible spalling and leaping quartz aggregates on the surface upon exposure to the flame indicate that the temperature exceeds the quartz inversion temperature of 573 °C. By placing thermocouples in different depths of the concrete sample, the surface temperature was estimated to 400 up to 600 °C, decreasing rapidly with depth.

![Figure 1: a) Application of glass onto concrete specimen by flame spraying [1]; b) NMR-MOUSE PM5, used for experiments](image)

For single-sided NMR measurements, a NMR MOUSE PM5 (Mobile Universal Surface Explorer) [7] with a maximum measurement depth of 5 mm was used, shown in Figure 1b). Employing a CPMG sequence with 300 echoes, a pulse length of 0.009 ms, a time between echoes of 0.033 ms, an acquisition time of 0.005 ms, and a waiting time of 500 ms, 1024 subsequent scans were measured and averaged. The so-called sensitive volume, from which information is gathered using these settings, is 20 x 20 x 0.1 mm³. To gain depth depending information, the magnet array was moved by a stepping-motor in 0.1 mm steps in a range of 0 mm (specimen’s surface) to 5 mm (specimen’s inside). Before measurement, the specimens were saturated with water and, to prevent the specimens from drying while measuring, they were wrapped into polyethylene foil.

For data evaluation, first the recorded amplitudes were divided by the amplitude of pure water, recorded with a waiting time of several seconds, ensuring that all spins contribute to the signal amplitude. Furthermore, two ways of data evaluation were employed. First, a tri-exponential decay function was fitted to the data using a least-squares algorithm. Second, an algorithm for inverse laplace transformation (ILT) was used, transferring the time-domain data into a distribution of exponential relaxation-times $T_2$. Within the algorithm, the range of relaxation times was chosen between 0.1 and 300 ms with a total of 100 summands. The regularisation parameter (alpha) was set to $10^9$.

3 Results

The exposure of the concrete sample to the high temperature flame leads to a damage of the near surface concrete structure. Looking at the microscopic image in Figure 2a), the concrete surface appears highly damaged, showing cracks around and inside the quartz aggregates as well as in the cement stone. As a consequence, the specimen failed at a pull-off strength of 0.15 N/mm², which is approx. 5 % of the original pull-off strength of the untreated concrete
sample. The fractures in Figure 2b) show mostly adhesive failure between concrete and glass, while some quartz aggregates partly adhered to the glass coating.

Figure 2: Specimen a) in optical microscopy and b) after adhesion testing

Figure 3a) shows the decaying NMR-signals, obtained from the sample at the surface (2.1 to 2.5 mm) and the inner material (4.6 to 5.0 mm). Figure 3b) shows the T₂-distributions, obtained by transferring the decaying signals into relaxation-time domain by ILT. In the latter T₂-distribution, the three relaxation times of 0.3, 1.5, and 10 ms can be related to relaxation times, reported in [6], and are attributed to gel, interhydrate, and capillary/air void porosity, respectively. Since the heat in the concrete during flame spraying acts mainly on the surface and decreases very rapidly with increasing depth, it can be assumed that the depth range of 2.1 to 2.5 mm is exposed to a high temperature while the greatest depth range from 4.6 to 5.0 mm is only exposed to a fraction of that heat. Due to the temperature exposure, the first peak at approx. 0.3 ms decreases in amplitude while shifting to slightly higher relaxation times. The second peak at approx. 1.5 ms shifts to longer relaxation times as well but remains at an similar amplitude. The third peak at approx. 10 ms increases in size and amplitude for the sample.

Figure 3: a) Relaxation signals and B) ILT-T₂-distributions close to the specimen’s surface (2.1 to 2.5 mm) and the inner material (4.6 to 5.0 mm)

The results indicate that with increasing temperature exposure, gel porosity in the cement stone is reduced while its pore size is slightly increased, shown here by decreasing peak area
and increasing mid relaxation time. Interhydrate pores increase in size, while staying relatively constant in volume. Furthermore, capillary and void porosity is increased several times. The results are in good accordance to the effects described in the literature [3].

4 Conclusion
Being able to measure the change of porosity in the cover zone non-destructively paves the way for a number of ground breaking new applications in research and for on-site testing in rehabilitation and repair.

- In this proceeding, it was shown that with single-sided NMR, the damage in concrete due to high temperature exposure can be measured with a depth resolution of 0.5 mm allowing the identification of surface defects, its depth influence, and separating these effects from bulk damage.
- In the mutually effort of the two institutes – ibac and GHI – further improvement on the application process by flame spraying must be made to enhance adhesion while reducing permeability of the glass layers.
- Mobile single-sided NMR, such as the NMR device used, has already and will in future show itself useful for non-destructive evaluation of concrete structures in the laboratory and on site. In particular, effects of thermal exposure, e.g. after a fire event, and its influence on concrete surfaces and bulk material can be evaluated with a high depth resolution, allowing controlled and customized removal and retrofitting of damaged concrete surfaces.

Acknowledgement
The authors would like to thank the German Research Foundation for the funding of the project and Petrik Galvosas, School of Chemical and Physical Sciences, University of Wellington, and his working group for providing the ILT algorithm, used in this work.

5 Literature