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The Potential of Nuclear Magnetic Resonance (NMR) to Non-Destructively Characterize Early-Age Concrete by an One-Sided Access (OSA) Technique

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Abstract

For in-situ inspection of concrete, there is generally a considerable pent-up demand in measuring non-mechanical quantities of building materials. Special interest applies to methods characterizing the properties of moisture storage and transport, because water influences nearly all damage processes in concrete. Determining these properties in-situ offers the possibility to describe the drying process in a component and to predict its sensitivity for pollutant absorption in order to prevent fatal damage in service-life of a construction. There is also a strong need for characterizing the very early life of concrete, when its strength develops and water binding processes are dominant. Hydrogen nuclear magnetic resonance (^{1}H-NMR) is an appropriate tool to determine water interactions with solid materials due to its sensitivity to hydrogen. Conventional NMR techniques are exclusively used as laboratory technique comprising a large, sophisticated instrumentation and requiring a detailed expert knowledge for operation. In contrast, „NMR-INSPECT" represents the worldwide first completely portable, battery-powered measuring system based on ^{1}H-NMR. It allows application from a single side to the specimen. At present, this is the only available method for completely non-destructive detection of depth-resolved water content and mobility. With this instrumentation it is possible to recognize the risk for a reduced residual life time of building materials at very early times. Besides it could help to accurately control concrete work (production and mixing) as well as to monitor workability and strength development after setting.

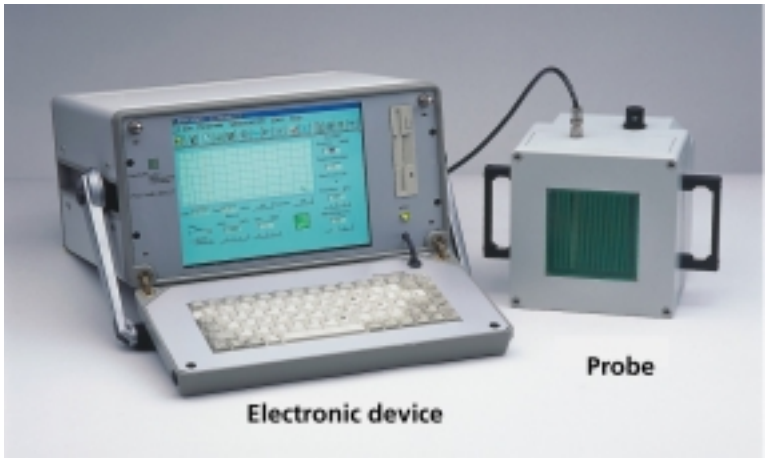

Figure 1: NMR-INSPECT

1. Introduction

Fresh concrete develops in strength over time. Initially, after casting, the concrete is supported within formwork until it gains sufficient strength to support its own weight. Early age damage as well as increased susceptibility to detrimental influences from the environment (reduced durability) can often be traced to insufficient strength development prior to loading of the structure.

The development of mechanical properties in concrete is closely related to the chemical reaction between cement and water - a process called hydration. During hydration the matrix phase of concrete, the so-called cement-stone is formed. Cement-stone is a nano-structured material; the oldest and as far as quantity is concerned the most important. The macroscopic strength of concrete is a consequence of an irregular structure of nano-crystallites in the cement-stone. Water is an important structural component of cement-stone. On one hand it is chemically bound in the crystallites and on the other hand it is physically adsorbed to the huge internal surface as a part of the gel pore phase. Besides, water is also bound in larger capillary pores, which are responsible for the moisture transport and the permeation of substances (e.g. water, aggressive ions) from outside into the internal structure of concrete.

In early life of concrete, the information about the microstructural properties of concrete is essential in order to observe the development of macroscopic properties (strength, durability) as well as to predict their values in the hardened state. Gaining microstructural information as with optical microscopy, REM, a.s.o. is usually incorporated with extensive, time-consuming laboratory measurements, which require destructively prepared samples (e.g. cutting, drying and polishing of the sample). Especially in case of “developing” materials as fresh concrete, this sample preparation can drastically affect the microstructure. Nuclear magnetic resonance (NMR) is a measuring method, which allows acquiring structural information in porous materials in a “non-invasive” manner. That means, there is no need for a preparation procedure eventually modifying the microstructure and usually the measurement is fast enough to prevent significant changes of material properties.

Traditionally, NMR is a typical laboratory technique comprising a large, sophisticated instrumentation and requiring a detailed expert knowledge for operation. Due to the fact, that the sample has to be inserted into the limited interior of the NMR equipment, its application on solid materials is usually restricted to small samples ($< 1\ cm^3$). In regards to concrete, this “old-fashioned” NMR can be used for principal investigations of chemical and physical processes during hardening and for basic quality assurance in the framework of material development (e.g. “high performance concrete”, new additives).

A completely different instrumental approach is required, if NMR should be applied in situ, for instance to check the drying state and the hardening degree in a freshly cast cement floor. In this case, a portable, robust and easy-to-use instrumentation is needed, which can be applied in one-sided access (OSA) to the test object. In a co-operation between the Fraunhofer-Institut fuer zerstoerungsfreie Pruefverfahren (IZFP) and QNET - Quality Management GmbH the worldwide first completely portable, battery-powered and one-sided NMR equipment, called „NMR-INSPECT” was developed. At present, this instrumentation represents the only really non-destructive method for characterizing the content, the bonding and the transport of water in concrete.

2. Physical background and instrumentation

2.1 Nuclear spin and magnetization

^{1}H-NMR is a spectroscopic technique, which uses the resonance interaction between electromagnetic waves and hydrogen nuclei placed in an external magnetic field. There are a number of excellent monographs describing the physical principles of NMR in detail [1, 2]. NMR is based on the nuclear spin, which is a quantum mechanical property of certain isotopes, as hydrogen (^{1}H), fluorine (^{19}F), carbon (^{13}C) and others. This spin results in a magnetic dipole moment, which aligns with an applied external magnetic field, generally labelled as $\vec{B}_0$ (see figure 2b). Additionally, the spin axis can be thought of as precessing, or revolving around the direction of $\vec{B}_0$. The speed at which the axis rotates is the precessional frequency or Larmor resonance frequency. This frequency is directly proportional to the external field strength with a proportionality constant called the gyromagnetic ratio γ, $\omega_0 = \gamma \cdot B_0$. The gyromagnetic ratio is fixed for each different type of atomic nuclei.

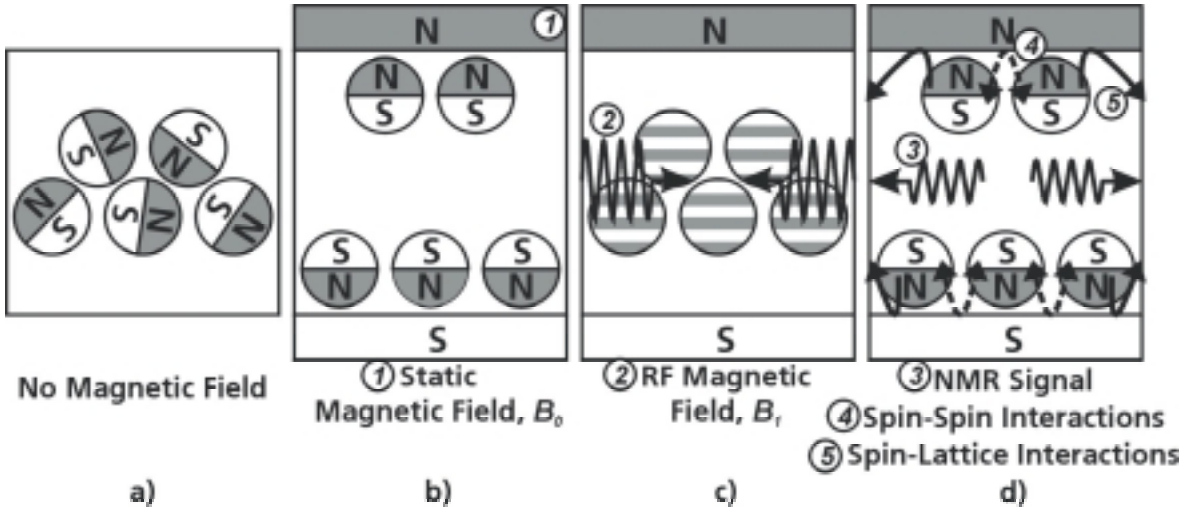

Figure 2: Physical principles of Nuclear Magnetic Resonance.

In an object volume with a large number of spins, part of the nuclear dipole moments are aligned in the direction of the external magnetic field and part are exactly the opposite. The former is a lower-energy state and the latter is higher. The vector sum of all moments gives the net magnetization in the object volume. In thermodynamic equilibrium this magnetization is parallel to the external magnetic field and therefore it is called longitudinal magnetization. The spins will be induced to resonant absorb and afterwards emit energy by applying electromagnetic energy at the Larmor frequency. This electromagnetic field will change the number of nuclei in the two energy states (see figure 2c). The longitudinal magnetization is transferred into transversal magnetization. For magnetic fields between 10^{-2} and 10^{1} T, which is typical for most NMR experiments, the Larmor frequency is in the MHz range, in consequence of which the applied electromagnetic field is often called radiofrequency (rf) field.

2.2 Pulsed NMR

In pulsed NMR the rf field is applied as a transient pulse, which is described by its amplitude magnetic field vector $\vec{B}_1$ and its duration t_p. Usually, a coil which is part of a resonant circuit transmits one or more such rf pulses to the object volume. After tuning off the pulse(s), the emitted energy is measured as an alternating voltage induced in the same (rf) coil. The amplitude of this NMR signal is proportional to number of resonant spins in the observed object volume. But the absorbed excess energy is also dissipated due to interactions between the spins and their atomic and molecular environment (spin-lattice interactions) as well as due to interactions of the spins among each other (spin-spin interactions). These interactions are modulated in time by molecular motions giving rise to two relaxation processes (see figure 2d). Phenomenological, a gradual recovery of the longitudinal magnetization is observed as well as a gradual loss of transverse magnetization. The former process is labelled as T_1 relaxation and the latter as T_2 relaxation. In the simplest case, each process proceeds exponentially in time. Then, it is described by a single time-constant, i.e. by a single relaxation time T_1 and T_2 respectively.

2.3 Spatially resolved NMR

Spatially resolved NMR (Magnetic Resonance Imaging, MRI) is based on the proportionality between the Larmor frequency and the magnetic field strength. In a spatially varying magnetic field each volume element will be characterised by a specific Larmor frequency according to the local magnetic field. Therefore the frequency spectrum of the received signal can be directly translated into a corresponding spatial signal distribution. The spatial encoding in one direction is accomplished by a magnetic field strength, which shows up a gradient G in this direction. Now, a sensitive slice can be selected at any point in this direction by choosing the frequency of the rf pulse to correspond to the Larmor frequency at this point. The 2D spatial reconstruction in this slice is accomplished using additional gradient fields in other directions (see figure 3a).

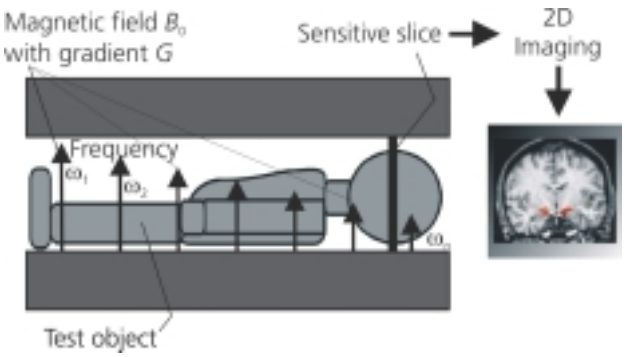

Figure 3a: Conventional MRI instrumentation.

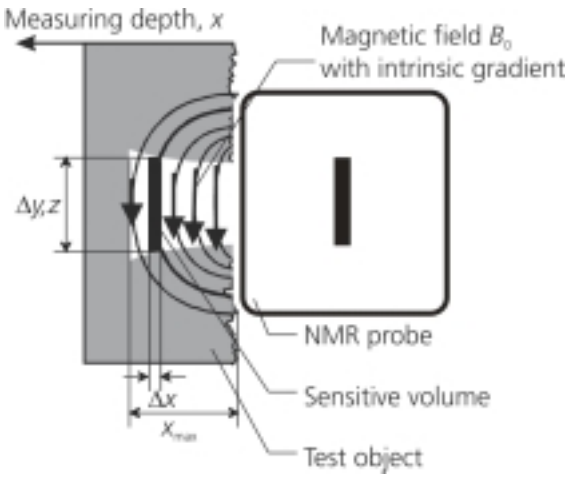

Figure 3b: OSA-NMR.

2.4 Instrumentation - Conventional NMR and one-sided access NMR (OSA-NMR)

The principal components of a NMR instrumentation are the magnet assembly providing $\vec{B}_0$ and the rf coil, which generates $\vec{B}_1$. In case of imaging NMR, additionally some gradient coils serving for the gradient fields are needed. For conventional NMR, these components are arranged in an enclosing apparatus, in which the sample has to be inserted. Therefore the size of the sample is restricted (see figure). In case of large test objects, e.g. building constructions, it is necessary to take a sample, i.e. to damage the object. Repeated measurements at the same position of the object - e.g. in order to monitor the hardening process in a concrete wall - are not possible.

One-sided access (OSA) NMR is accomplished by using the outer stray-fields instead of the inner fields of magnet assembly and coil. Numerical optimized designs of an U-shaped magnet assembly and a flat coil provide for a highly efficient $\vec{B}_0$ and $\vec{B}_1$ generation outside to the NMR probe (see figure 3b). The external magnetic field shows a strong intrinsic gradient perpendicular to the probe surface. Hence, spatially resolved NMR signals can be measured without any additional gradient coils as they are necessary in case of conventional NMR. Again, a sensitive slice or sensitive volume can be selected. It is parallel to the probe surface and its depth position depends on the frequency of the rf pulse. Its thickness and with it the resolvable depth-increment can be varied between 0.5 and 2 mm. By gradually shifting this sensitive volume through the test object, the measuring depth can be varied between surface of the test object and the maximum measuring depth, x_{max}. In this way, depth-profiles of NMR signals can be detected. At present x_{max} is restricted to approximately 20 - 30 mm. The restriction is not a physical limit but rather a practical limit designated by the signal-to-noise-ratio, which gradually drops with increasing measuring depth. The further development of OSA NMR is directed to increase x_{max} up to values of about 100 mm.

3. The potential of NMR for concrete characterization

Investigations of cement based materials with NMR are known for almost 50 years. Only 10 years after the discovery of NMR phenomenon in bulk matter, this method was used to determine the ratio of crystal water to free water in a cement paste [3]. Nowadays, the enormous potential of NMR methods for concrete characterization is well explored and described in monographs [4].

3.1 Water content measurements

As described in section 2, a ^{1}H-NMR experiment yields two types of measuring information. The signal amplitude is a measure for the quantity of hydrogen (hydrogen density). In a moist material, the hydrogen density is directly proportional to the overall water content within the detected object volume (see figure 4). NMR is a well established method for fast and accurate moisture determination in pharmaceutical, cosmetic and foodstuff industry [5]. Successful aquametric applications have also been reported in technical materials as concrete, wood and polymers [6]. Accuracies better than 0.2 % have been achieved [7]. Even if the material contains other hydrogenous substances besides water, it is still possible to accurately determine the moisture content [8].

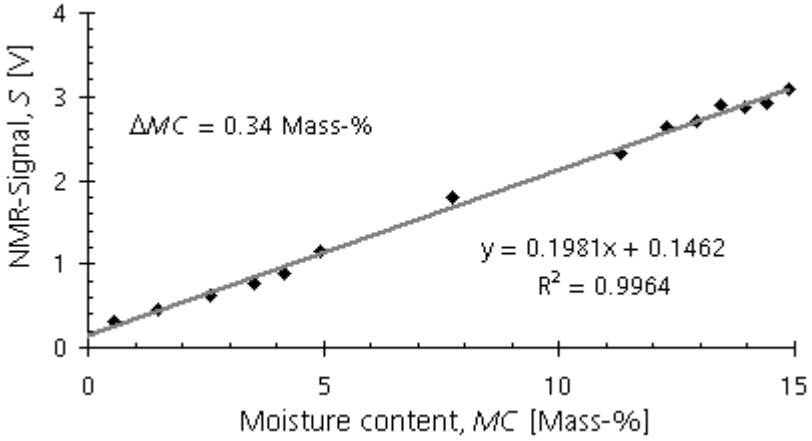

Figure 4: Water content measurement in light-weight concrete with NMR; Calibration to gravimetric (destructively) determined moisture content.

3.2 Water mobility measurements

Additional information can be revealed from the analysis of the relaxation processes. In general, these processes are highly sensitive to molecular dynamics (hydrogen mobility). By means of the relaxation times T_1 and T_2, chemically combined water can be distinguished from water, which is physically bound to a solid surface and water, which is in the bulk liquid state. During hardening of cement stone, more and more water is chemically combined in hydration products, small gel pores are developing at cost of large capillary pores. Hence, the water mobility in concrete is changing continuously, originating a pronounced effect on the relaxation times (see figure 5a). A detailed relaxation analysis allows determining the relative portions of hydrogeneous phases in concrete, which are the chemically bound water (water of hydration) with a T_1 less than 10^{-4} s, the water in gel pores with a T_1 in the of 10^{-3} s range and the loosely bound water in capillary pores with a T_1 of about 10^{-2} s [9]. This offers the possibility to observe the development of these phases during hardening (see figure 5b).

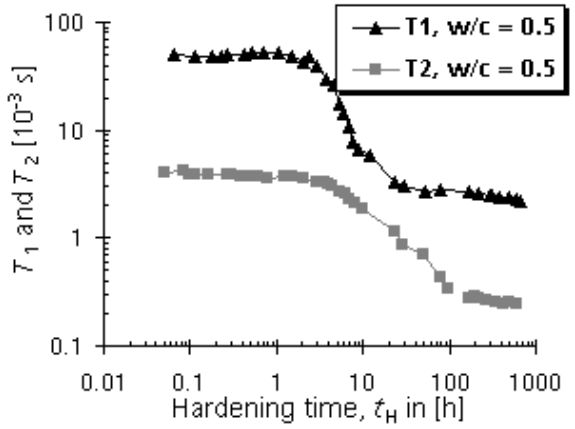

Figure 5a: T_1 and T_2 measured in a cement paste with w/c = 0.5 (water-to-cement ratio) as function of hardening time.

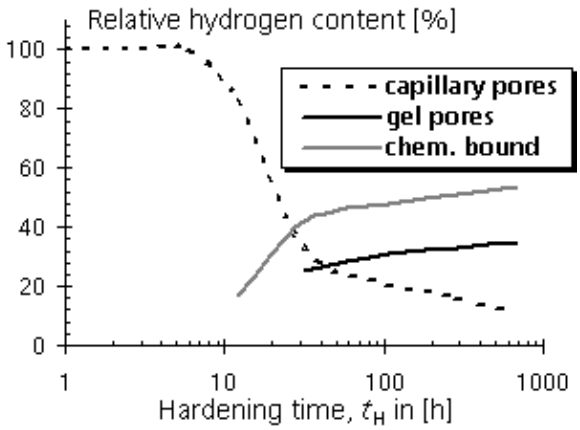

Figure 5b: Hydrogen amount in capillary pores, gel pores and chemically bound water as a function of hardening time.

4. Applications of one-sided access NMR (OSA-NMR)

With OSA-NMR a moisture content profile can be measured non-destructively with a resolvable increment in the mm-range. This offers the possibility to monitor water absporption / desorption and moisture migration during drying and wetting processes. The ability to do this in-situ allows to investigate the drying process in a component and to predict its sensitivity for pollutant absorption preventing fatal damage in service-life of a construction.

4.1 Drying and shrinkage in cement floors

The drying monitoring in cement floors is an instructive example for the practical benefits of depth-resolved moisture measurements with OSA-NMR. Cement floors often tend to be dimensionally unstable due to inhomogeneous shrinkage during the process of simultaneous hardening and drying. Crack formation is another serious damage mechanism supported by inhomogeneous shrinkage. In order to investigate the interrelationship between shrinkage and drying, the distribution of evaporable moisture in different plaster mixtures was monitored with OSA-NMR. Simultaneous the shrinkage bend of the mixtures was measured.

Fig. 6 shows a three-dimensional representation of the development of the moisture distribution within a typical cement floor over a period of 161 days after setting. One specimen was sealed at the surface with a water-proof plastic sheet for 14 days (right picture). In construction work, this post-curing is a well-established method in order to enhance the performance of cement-based materials. However, as it was enlightened in our studies, the post-curing retards the drying process and supports amount of unwanted shrinkage.

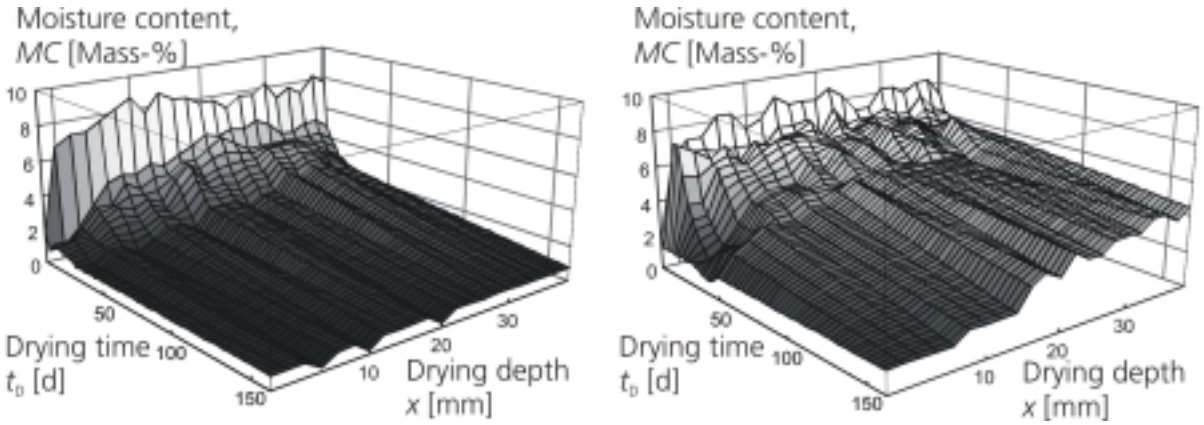

Figure 6: Development of moisture distribution in on-sided drying cement floor; the drying surface is at x = 0 mm; standard specimen (left) and post-cured specimen (right).

4.2 Moisture penetration depth in concrete

Many durability problems of building materials such as frost attack, embedded steel corrosion, timber rot and fungal attack are associated with high moisture levels. To evaluate the risk of a moisture induced damage resulting in a diminished durability, it is necessary to determine the water transport properties of these porous materials [10]. The water permeability is a key property required in order to predict the service life of a building

component. Measuring the moisture penetration depth as a function of time with OSA-NMR gives a good estimate of this water permeability (see figure 7a). Since the method is contact-less, it is also applicable on components with pronounced surface roughness (see figure 7b).

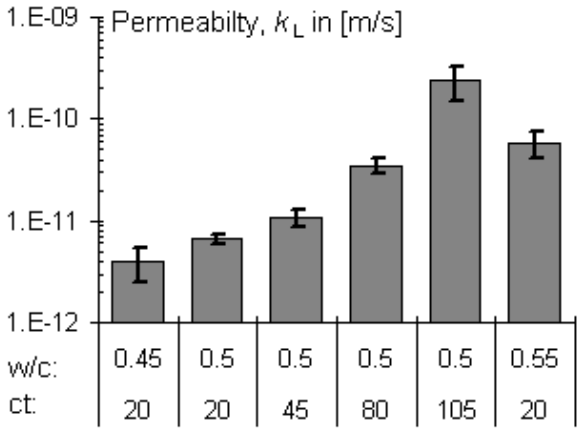

Figure 7a: Water permeability in concrete, determined from time-dependent moisture profile measurements with OSA-NMR; concrete specimen with different water-to-cement ratio (w/c) and different curing temperature (ct) have been investigated.

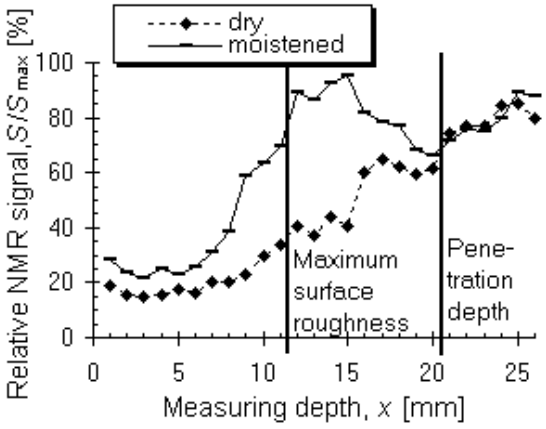

Figure 7b: Determination of the water penetration depth in concrete with pronounced surface roughness after 30 min moistening from the left side (x = 0 mm); Note: the penetration depth results from the relative signal gain after moistening.

4.3 Concrete hardening

Event though a variety of methods to measure the properties of fresh concrete are already available, monitoring the strength development in early-age concrete is still an unsolved testing problem. Conventional methods, as for example the Vicat needle test, the slump test, the flow table test a.s.o. are not objective because the results are highly dependent on the measuring device and the measuring procedure. None of these methods allows continuous monitoring of material properties from the fresh until the hardened state, because they are destructive.

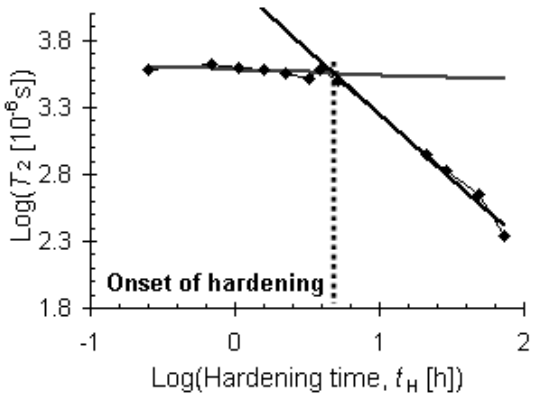

Figure 8a: Determination of the onset of hardening with continuous T_2 measurements.

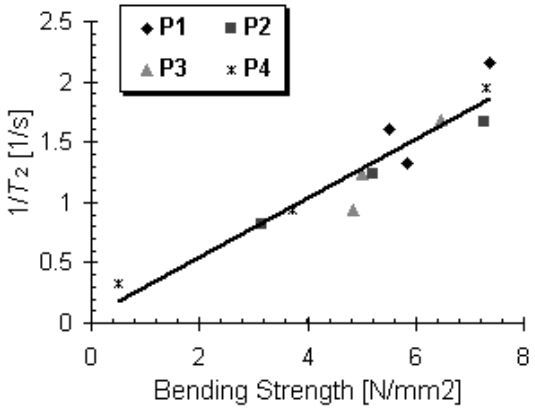

Figure 8b: Reverse relaxation time T_2 as a function of bending strength in mortars.

Measuring the NMR relaxation of hydrogen in concrete is a new approach, which allows continuous monitoring of concrete properties (see figure 8a). Investigations on different mortar mixtures have shown a clear correlation between NMR measuring signals and the (bending) compressive strength, which was determined with a destructive reference method (see figure 8b).

5. Conclusions

For a long time, nuclear magnetic resonance (NMR) instrumentation was found only in laboratories of institutional and industrial research facilities. Nowadays, special NMR equipment is available, which is one-sided accessible, hence allowing the nondestructive inspection of large objects. NMR-INSECT is portable, robust and easy-to-use device which is based on this OSA-NMR approach. It combines the large potential of NMR with an instrumental design, fulfilling the requirements of non-destructive testing on building-sites. The experimental results have shown, that OSA-NMR is a powerful tool for determining a variety of moisture related concrete properties. Spatially resolved measurements of the moisture content provide an unique possibility to characterize drying and wetting processes in building materials and with it to recognize the risk for a reduced residual life time at very early times - a clear progress in the light of structural safety. NMR relaxation measurements could help to accurately control concrete work (production and mixing) as well as to monitor workability and strength development after setting. For the first time, it is possible to accurately determine the time for demolding or removal of formwork in-situ. Further applications arise from the identification of early stiffening and flash set in ready-mix suppliers.

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