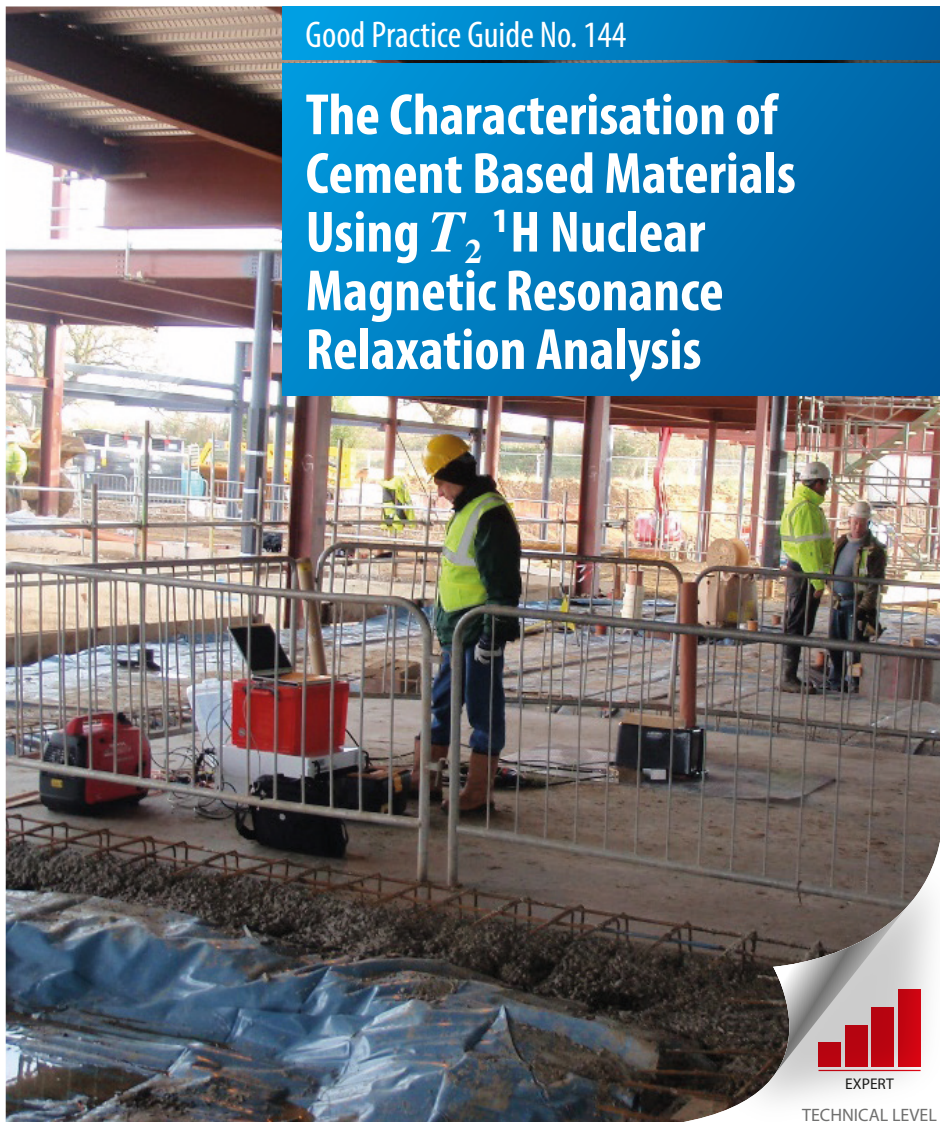




Good Practice Guide No. 144

The Characterisation of Cement Based Materials Using T_2 ^1H Nuclear Magnetic Resonance Relaxation Analysis



EXPERT

TECHNICAL LEVEL



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Front cover image: *On-site NMR being employed during construction of a swimming pool. (Source: P. McDonald, University of Surrey).*

Guide Information

What is it about?

This Guide is an introduction to the basic concepts of using ^1H nuclear magnetic resonance (NMR) relaxometry to determine the state of water in cement, and hence the degree of cure of the cement and the cement microstructure, in particular the porosity. The Guide provides information on calibrating the equipment, the NMR responses that can typically be found from cement and how to quantify the information obtained. Recommendations are made for the specification of suitable equipment, the set-up procedures required, and the experiments to be performed. Detailed results of an international Round Robin Trial are included to demonstrate the usability, repeatability and accuracy of the method. The preparation of suitable non-cementitious reference materials is also discussed.

Who is it for?

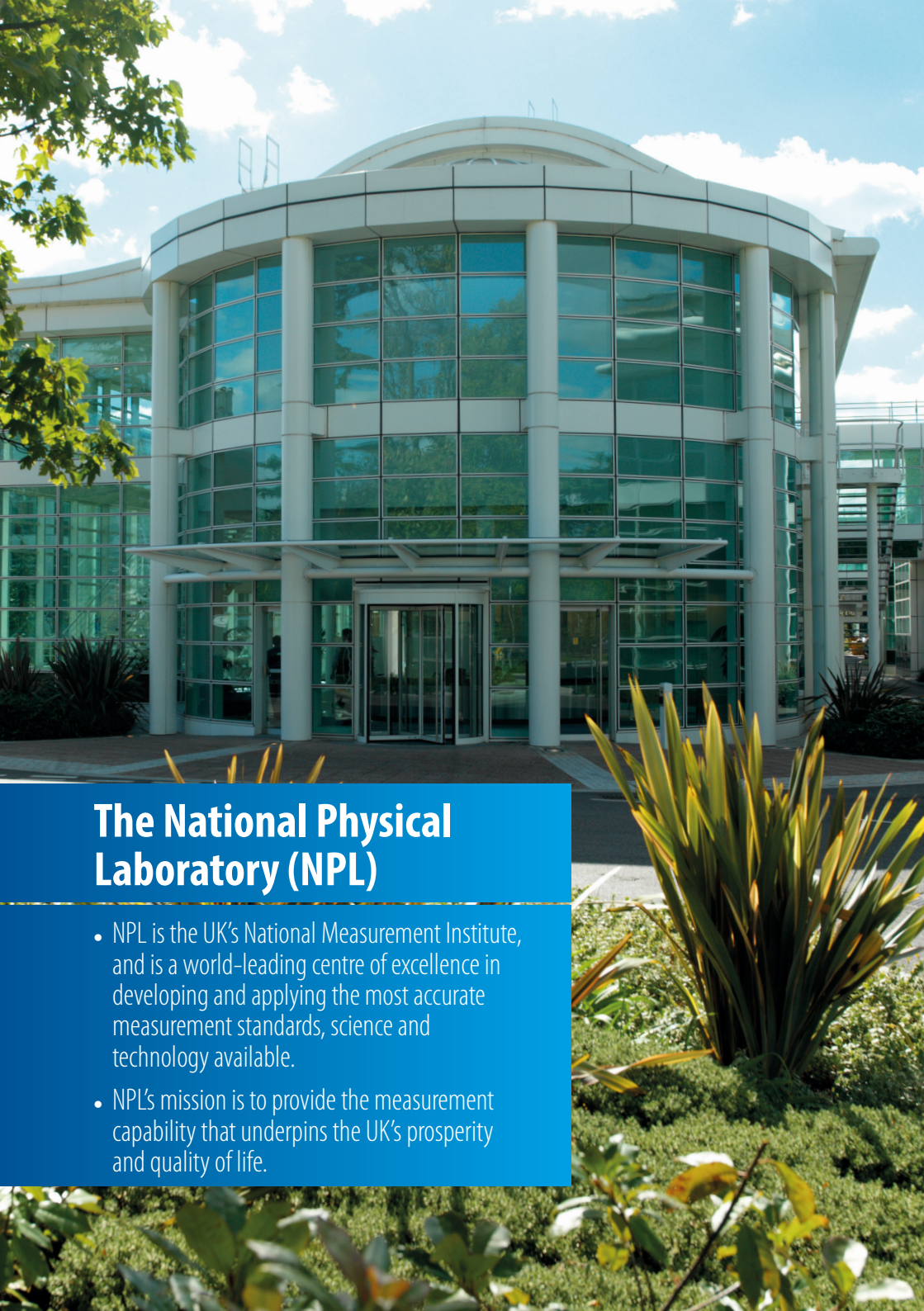
This Guide is intended for materials scientists and technologists in the cement and cement additive production industry, as well as those involved in the characterisation of cements of existing structures and during new build. It is also of value to non-NMR specialists seeking to use NMR as a cement characterisation tool in academia, standards laboratories, buildings test facilities, and similar organisations. The Guide will also assist those seeking to design and manufacture NMR equipment targeted at the cement industry. Finally, those looking to introduce NMR for the study of alternate porous media will find highlighted many of the general pitfalls associated with the technique.

What is its purpose?

This Guide is intended to promote the concept of NMR as both a research and a quality assurance tool, and to encourage the design and manufacture of suitable equipment for both laboratory and field use.

What is the prerequisite knowledge?

This Guide assumes a moderate level of physics background, as well as some understanding of cement chemistry.



The National Physical Laboratory (NPL)

- NPL is the UK's National Measurement Institute, and is a world-leading centre of excellence in developing and applying the most accurate measurement standards, science and technology available.
- NPL's mission is to provide the measurement capability that underpins the UK's prosperity and quality of life.

Foreword

This Guide is largely the result of more than ten years study by researchers at the University of Surrey (www.surrey.ac.uk) led by Professor Peter McDonald and colleagues within the Nanocem Consortium (www.nanocem.org) who, at its inception, saw the potential for ^1H nuclear magnetic resonance to provide new and important information on the microstructure of cement, on its hydration, and on pore–water interactions within it.

This potential is now being fulfilled, with the number of users in cement science and engineering growing sharply. However, whereas previously measurements were often made by experts in NMR, perhaps with little experience of cement science, the reverse is increasingly true. A growing number of users are experts in cement science, but with little experience of NMR. In addition, instrumentation manufacturers are now starting to develop bespoke equipment and are seeking guidance on the technical requirements of the analysis. These are the primary reasons for the development of this Good Practice Guide.

The involvement of NPL goes back just two years. First, the University of Surrey researchers realised that stable and reproducible reference materials that mimicked the (rather unusual) relaxation behaviour of cement were required to test instrumentation and analysis procedures. Finding such materials was non-trivial. They also realised that a rather different route to non-expert NMR users was required to disseminate good practice in terms of ‘dos and don’ts’ than the traditional peer-reviewed academic publication. Second, about the same time, the University as a whole entered a strategic partnership with NPL that facilitated collaboration. Consequently, the Surrey researchers approached Roger Morrell at NPL for help both in developing reference materials and in disseminating good practice. This Guide is the result.

Peter McDonald

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List of abbreviations and symbols

Abbreviations:

CPMG	Carr-Purcell-Meiboom-Gill multiple spin-echo experiment for measuring T_2
DSV	Diameter of sample volume
FID	Free induction decay
FOV	Field of view
ILT	Inverse Laplace transform
MRI	Magnetic resonance imaging
NMR	Nuclear magnetic resonance
Spin-echo	Refocused signal observed after the application of two or more excitation pulses
SNR	Signal to noise ratio

Cement chemistry symbols:

C	CaO in cement chemistry notation
S	SiO ₂ in cement chemistry notation
H	H ₂ O in cement chemistry notation (but note that ¹ H represents hydrogen for NMR purposes)
A	Al ₂ O ₃ in cement chemistry notation
$\bar{C}$	CO ₂ in cement chemistry notation
$\bar{S}$	SO ₃ in cement chemistry notation
F	Fe ₂ O ₃
C-S-H	Calcium silicate hydrate
C-A-S-H	Calcium aluminium silicate hydrate
CH	Calcium hydroxide, portlandite
Ett	Ettringite, C ₆ A $\bar{S}$ ₃ H ₃₂

Mathematical symbols:

α	Regularisation parameter in ILT fitting
β_x	The inverse mass fraction of water in x
$\mathbf{B}_0$	The applied static magnetic field taken as defining the Oz axis of the experiment
$\mathbf{B}_1$	The radio frequency excitation magnetic field applied along the x' or y' axis of the reference frame rotating about $\mathbf{B}_0$ at the resonant frequency
D	Diffusion coefficient
Δ	Time between two gradient pulses in a diffusion experiment
δ	Duration of a gradient pulse
E	Energy
f_0	NMR frequency
f_s	Data sampling frequency
f_y	Mass fraction of y
g	Magnetic field gradient strength
Γ	Torque
γ	Magnetogyric ratio
$\hbar$	Planck's constant h divided by 2π
ϑ	Temperature
θ_p	Phase angle
I_x	Signal fraction attributed to water in microstructure x
M^0	Equilibrium magnetisation
$M_{R/I}$	Magnetisation in the real/imaginary detector channels
$M'_{R/I}$	Magnetisation in the real/imaginary detector channels of phased data
m_y	Actual mass of y
m_y^x	Actual mass of y in microstructure x
μ	Magnetic moment
N	Number of points
n_s	Number of scans
$\mathbf{P}$	Angular momentum
P, P_0	Pressure, saturated water vapour pressure
P_{90}	NMR pulse of 90°
P_{180}	NMR pulse of 180°
R_G	Gas constant

r	Position
r_c	Maximum size of a pore in which liquid water condenses
σ	Surface tension
t	Time
t_d	$1/f_s$
t_{min}	The time of the first echo
t_{max}	The time of the last echo
t_{p90}	Length of a 90° pulse.
t_{p180}	Length of a 180° pulse.
T_1	Nuclear spin lattice relaxation time
T_2	Nuclear spin-spin relaxation time
T_2^*	Observed apparent nuclear spin-spin relaxation time of a signal observed following a single 90° excitation pulse
T_2^{AB}	Signal decay time in an inhomogenous magnetic field of average inhomogeneity ΔB
T_2^{eff}	An effective T_2 due to for instance diffusion in a magnetic field gradient
τ	Pulse gap between the 90° and 180° pulses in a spin-echo or CPMG experiment. The first echo occurs at 2τ
τ_q	Pulse gap used in the solid echo experiment
τ_{RD}	Repetition delay between scans (from the start of one scan to the next) used for signal averaging.
τ_{sat}	Delay between saturation and inspection pulses of the T_1 saturation recovery experiment.
τ_{inv}	Delay between inversion and inspection pulses of the T_1 inversion recovery experiment.
τ_1	The first P_{90} to P_{180} pulse gap in a CPMG experiment, so that $2\tau_1 = 2\tau_{min}$ is the first echo time
τ_N	One half of the last P_{180} to P_{180} pulse gap in a CPMG experiment, so that $2\tau_N = 2\tau_{max}$ is the last echo spacing
x, y, z	Coordinates of the NMR laboratory frame of reference with Oz aligned along $\mathbf{B}_0$.
x', y', z'	Co-ordinates of the NMR rotating frame of reference
Y^{AMU}	Mass of Y expressed in atomic mass units
Y_X^{AMU}	Mass of Y in X expressed in atomic mass units

Chapter I

Introduction

- Background to this Guide
- Why use NMR to characterise cement based materials?
- Historical origins

Background to this Guide

Nuclear magnetic resonance (NMR) relaxometry of hydrogen is widely used to characterise many industrially important porous materials such as rocks for petroleum reservoir exploration (including down bore-hole), foods and pharma for quality assurance. Most recently it has come to the fore as a powerful tool to characterise cement based materials. ^1H NMR is able to quantify the amount of water used in the formation of crystalline phases, included in gel hydrates, and also found filling capillary pores of different sizes. As such, NMR can be used to assess the amount of hydrates that have formed and provide a measure of the state of cure of the material. It can also be used to characterise the microstructure that has evolved, and to measure the pore size distribution. With the advent of modern electronics, high performance permanent magnets and digital signal processing, NMR is seen as routine and affordable requiring only bench top, or even transportable, equipment. With the addition of magnetic field gradient coils to the equipment, spatially localised measurements - “imaging” or “MRI” - and molecular diffusion analyses are possible. Imaging is used to map water profiles throughout materials, thereby facilitating the measurement of, for instance, permeability or allowing separate measurements of surface and subsurface properties. Molecular diffusion probes transport at the molecular level and can provide information of the connectivity of the porosity.

It is seen then that NMR characterisation of cements can be an extremely rich and rewarding science. However, the experiments can appear to be complex. Many variants of the basic methods are possible. This complexity leads to confusion in the interpretation of data. Variations in experimental parameters and analysis protocols can lead to variations in results that, without proper understanding, may be interpreted incorrectly or lead to apparent contradictions. In the case of cements, complexity extends to sample manufacture, preparation and history. Indeed, it is only recently that a self-consistent and full interpretation of cement ^1H NMR data has emerged from multiple studies in multiple laboratories worldwide. This has come about from detailed studies comparing the results of NMR to other methods including scanning electron microscopy, X-ray diffraction and thermal gravimetric analysis.

A further difficulty is that measured NMR characteristics of cement lie in an awkward region of parameter space outside that occupied by many other porous material systems. As a result, there has been a lack of stable and reproducible reference materials against which experimenters can validate their procedures. Again, it is only recently that good reference material analogues have been identified.

It is for the above reasons that it is felt that now is the appropriate time for this Good Practice Guide for ^1H NMR characterisation of cement. This Guide focuses mainly on relaxometry and specifically on measurement of the T_2 spin-spin relaxation time for phase-composition and pore-size distribution analysis. There is only brief mention of

the T_1 spin-lattice relaxation time, diffusometry and imaging. However, although these topics are not pursued in detail, much of the discussion of T_2 analysis carries across and forms a foundation of understanding upon which these other experiments may be carried out and interpreted.

The preparation of this Guide comes at the end of a Round Robin Trial involving twelve instruments of varying age and specification across eight European laboratories belonging to academic groups, cement manufacturers and instrumentation manufacturers. The trial informed elements of the good practice advocated in this guide and illustrated the range of measurement uncertainties to be expected under different experimental circumstances. Key results of the Round Robin Trial are presented in a later section, and full results are in Appendix F.

Why use NMR to characterise cement based materials?

^1H NMR used to characterise cement hydration and microstructure has three principal advantages compared to other methods. The first is that the water hydrogen inherent in the sample is, itself, the probe. This immediately negates any requirement to dry or otherwise prepare the sample. This is a significant advantage as the drying, and perhaps polishing or high pressure impregnation, required by other methods can disturb the delicate nano-scale structure of the cement hydrates. Turning this around, NMR relaxometry has been used to measure the pore size resolved sorption isotherm of cement ^[1] and to show exactly how the porosity evolves under cycles of drying and re-wetting ^[2, 3].

The second advantage is that the method is both non-invasive and non-destructive. As a result, repeat measurements and time-course studies, for instance during hydration, can be carried out. Using NMR, it has been possible to show how the development of porosity is non-linear with the degree of hydration ^[4] and hence to update Power's classic model of hydration ^[5].

The third advantage is that NMR relaxometry can be easy to perform. In its simplest form, the method comprises placing the sample inside a magnet and initiating resonance with a short pulse of radio waves. The sample "emits" a signal in response. In hydrated cements, the signal comprises different components of different intensity and decay time. Each component is identified with water in a different chemical or micro-structural environment. The intensity of the signal reflects the amount of water in that component, and the decay time reflects how mobile or confined the water is within it. In this way, water in crystalline solids is distinguished from water in hydrates and water in larger capillary pores, for instance. Beyond this simple experiment, however, is a very

rich array of further experimental possibility that can be brought to bear in order to investigate, for instance, the connectivity of the porosity^[6] or the transport of water within it^[7].

Key advantages of NMR

- Quantifies the principal components of hydrated cement - crystalline solids, hydrates, porosity.
- Quantifies the pore size distribution.
- Water is the probe.
- No sample drying or other preparation is required.
- Non-invasive and non-destructive.
- Time course studies on a single sample are possible.
- Can be a quick experiment.
- Can be performed on bench-top or portable equipment

Historical origins

The first NMR measurements of evaporable water in cement pastes were reported by Blinc *et al.* in 1978^[8]. These authors measured the so called ^1H T_1 and T_2 relaxation times of water in cement pastes during hydration from 10 minutes after mixing through to 28 days. Different stages of hydration were identified. However, Blinc *et al.* did not separate the signals into different components related to different microstructural environments. Schreiner *et al.*^[9] were amongst the first authors to make this advance. Experiments by Halperin *et al.*^[10] were amongst the first to use fast exchange theory^[11] and the idea of relaxation at surfaces to link the measured relaxation times to pore size and specific surface area in the cement. With time, most authors preferred to measure T_2 rather than T_1 because it is a more straightforward experiment and because the chemically combined water in crystalline solids is more easily separated from water in large pores. Greener *et al.*^[12] and Holly *et al.*^[13] studied T_2 relaxation in cement paste using a “cross normalised” combination of two NMR methods – a process akin to that adopted in this Guide – to increase quantification of the crystalline solids, and went on to identify five T_2 components. In ascending order of T_2 in the maturing paste, they are: crystalline solid; hydrate inter-layer water; hydrate gel pore water; capillary water; and water associated with ettringite to monosulphate conversion, although they noted that only the first four appeared in the mature paste. This assignment is compatible with the findings of Muller *et al.*^[4] who carefully compared NMR results with the results of other analyses including X-ray diffraction and thermogravimetric analysis in order to demonstrate how the

density of hydrates could be determined alongside the pore size distribution. In further work the same authors presented results from pastes incorporating silica fume ^[14] and demonstrated measurement of a pore size resolved desorption isotherm in cement paste ^[1]. Most recently, Fischer *et al.* ^[2] and Gajewicz *et al.* ^[3] have shown that, subsequent to drying and rewetting, the nanoscale porosity of cement and concrete is dynamic, evolving on a time scale of 1 - 2 days as gel pores that collapsed upon drying swell back to something approaching their original size.

Other significant work includes: $T_1 - T_2$ correlation and $T_2 - T_2$ exchange studies by McDonald, Korb and co-workers ^[6, 15] that measured the rate of water exchange between pores in fully saturated cement pastes; NMR cryoporometry in cement-based materials ^[16] that is relevant to studies of freeze-thaw; NMR diffusometry in cement pastes that probes micro scale molecular diffusion ^[17]; analysis of isopropanol - water exchange ^[18]; and applications of magnetic resonance imaging to study heterogeneity of curing and/or water transport ^[19, 20, 21, 22, 23]. These further analyses are largely beyond the scope of this Guide. However, reviews have been published by Korb ^[24], Valori *et al.* ^[25] and Muller *et al.* ^[26].

Principle of NMR applied to cements

- Introduction
- Resonance and the Larmor equation
- Excitation and the Free Induction Decay
- Nuclear spin relaxation: T_1 , T_2 and T_2^*
- Relaxation in liquids, pores and solids
- Improved experiments to measure T_2 and T_1 relaxation
- Imaging
- Diffusion analysis and q-space imaging

Introduction

NMR is a quantum mechanical phenomenon that requires a deep understanding of quantum mechanics for a complete and rigorous interpretation. However, for many applications, a simple but less rigorous classical picture suffices to describe the experiments. Both approaches are widely described in many admirable texts including those by Kimmich ^[27] and by Blümich ^[28]. The following description offers a very simplified, broad introduction. More detail of the vector model of NMR echo formation that underpins many of the experiments described here is offered in Appendix A.

Resonance and the Larmor equation

At its most basic level, a nuclear magnetic resonance experiment consists of placing a sample in a uniform magnetic field. Throughout this text, it is assumed that the sample contains hydrogen, ^1H , and that we are dealing with hydrogen NMR. Hydrogen is, of course, a key constituent of water, H_2O , denoted as H in cement chemistry notation. The proton nuclei at the centre of hydrogen atoms can be viewed as tiny bar magnets that align with the applied magnetic field so as to create an equilibrium bulk nuclear magnetisation in the sample. By convention, the field direction is used to determine the longitudinal, or z -axis, of the experiment. If the magnetisation is tilted away from this equilibrium alignment, into the transverse or x - y plane, then it precesses or rotates about the field. The effect is the magnetic analogue of a tilted gyroscope turning in a gravitational field. The frequency of the rotation, f_0 , is directly proportional to the strength of the field, B_0 . It is the Larmor or resonance frequency. It is given by the Larmor equation:

$$f_0 = \gamma / 2\pi B_0 \quad (1)$$

The constant of proportionality, $\gamma/2\pi$, is the magnetogyric ratio of the nuclei divided by 2π . For ^1H it is approximately 42.57 MHz/T.

Excitation and the Free Induction Decay

The initial energy required to tip the nuclei, and hence the magnetisation, out of alignment with the applied magnetic field is provided by a pulse of radio frequency energy transmitted into the sample at the resonant frequency. The energy comes from an a.c. current in a coil of wire wound around the sample, which creates an a.c. magnetic excitation field additional to the applied static field. The duration of the pulse, t_{pg} , is such as to rotate the nuclei through 90° and is typically a few

What kind of NMR is used to measure cements?

All NMR experiments exploit the fact that the probe atomic nuclei (e.g. the water hydrogen proton, ^1H) precess at a resonant frequency in an applied magnetic field. The resonance frequency is directly proportional to the field strength. Beyond this most simple description, there are broadly three kinds of NMR that have evolved historically: imaging, spectroscopy and relaxometry.

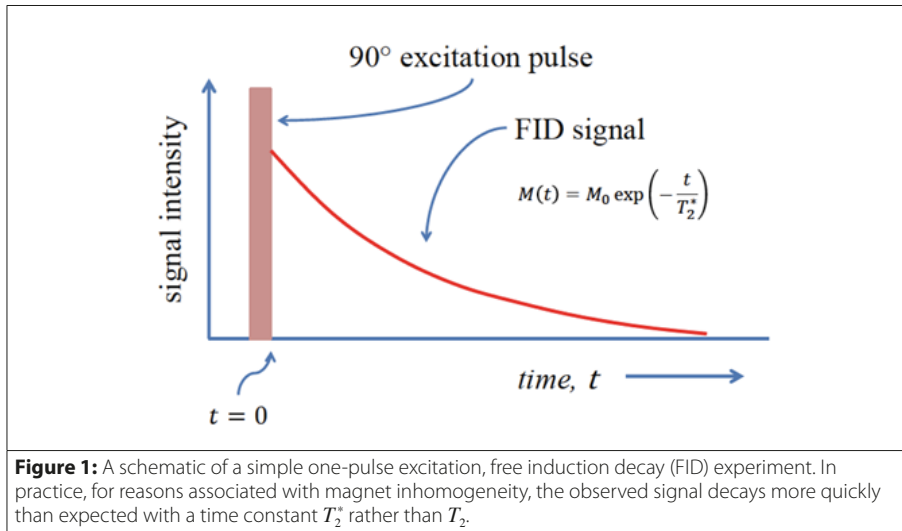
- **Imaging:** The most widely known form of NMR due to its pivotal role in medical diagnosis is magnetic resonance imaging (MRI). In MRI magnetic field gradients are superimposed on the applied, uniform, magnetic field. In this way the resonance frequency becomes a function of spatial position and so can be used to encode spatial information. Although MRI of cementitious materials is possible, most often to reveal the distribution of water across a sample, it is not a widely practiced method since it usually requires gradients stronger than those typically available in a medical scanner.
- **Spectroscopy:** A second kind of NMR is chemical spectroscopy. It is probably the most widely used in the laboratory. Here, the very small shifts in resonance frequency that arise from the magnetic interaction of one atom on another are used to reveal molecular structures. These shifts are at the level of parts per million (ppm). Spectroscopy is most common for molecules in solution, but is possible, though more difficult, for molecules in solids since, for solids, it is normally necessary to rotate the sample very rapidly during the measurement. In cements, spectroscopy is most often used to study Si–O co-ordination and the chain length of hydrates.
- **Relaxometry:** This is the third kind of NMR. Here the time dependence of NMR signals are studied in order to reveal molecular dynamics. In cements, it is almost exclusively applied to ^1H , especially to the ^1H associated with pore water. By this means it is possible to characterise the porosity of cement systems and the dynamics of water within that porosity.

microseconds. A 90° pulse is used since this maximises the projection of the magnetisation in the x - y plane orthogonal to the applied field along the z direction and hence maximises the magnitude of the subsequent signal.

Following the excitation pulse, the precessing magnetisation induces a signal in the form of an a.c. electric current at the resonance frequency in a detector coil of wire wound around the sample, just as moving a magnet induces a current in a solenoid. Most commonly, the same coil is used for detection as for excitation. The intensity of the signal, M_0 , is directly proportional to the amount of water in the sample. Normally, the signal M decays exponentially with time, t , so that:

$$M(t) = M_0 \exp\left(-t/T_2\right) \quad (2)$$

The signal lifetime, T_2 , properly known as the spin-spin or transverse relaxation time, serves as a measure of how mobile or confined the water is, as explained in subsequent sections. The signal is universally known as the NMR free induction decay, or FID for short. The application of a single pulse excitation and observation of an FID constitutes the most basic NMR experiment possible. It is shown schematically in Figure 1.



Once the signal has decayed, it is not immediately possible to repeat the experiment. To see why, consider again the FID. The precessing nuclei that make up the rotating magnetisation are initially all rotating together. However, each nucleus experiences a slightly different magnetic field compared to its neighbours due to magnetic interactions between the nuclei. As a result, all the nuclei precess at slightly different frequencies. In doing so, they lose coherence and de-phase. The net magnetisation, which is the vector sum of the individual nuclear moments in the sample, decreases and with it so does the signal amplitude. This is the origin of the T_2 relaxation. When all the nuclei point in different directions in the transverse plane, then no net current is induced in the detector coil and no signal is seen. However, the nuclei still lie in the x - y plane. They have not yet returned to where they started, in equilibrium alignment with the applied field along the z axis. This return to equilibrium is a second exponential relaxation process with a characteristic relaxation time known as the spin-lattice or longitudinal relaxation time, T_1 . It is always true that $T_1 \geq T_2$. Only when this time has passed may the experiment be repeated. The repetition time or delay is generally denoted τ_{RD} .

Nuclear spin relaxation: T_1 , T_2 and T_2^*

It was stated in the previous section that the FID decays with a time constant T_2 due to magnetic interactions between the nuclei that lead to variations in local magnetic field from one nucleus to the next. In practice, since all experiments are less than perfect, the FID actually decays with a time constant $T_2^* < T_2$. The further variations in local magnetic field experienced by different nuclei that lead to de-phasing and loss of signal on this shorter timescale have multiple origins, as outlined in the sections below.

Magnet inhomogeneity

Variations in the applied magnetic field with position r across the sample – magnetic field inhomogeneity – cause nuclei in different locations to precess at different rates. The severity of the field inhomogeneity is a function of the magnet quality, and hence is in no way a measure of the sample. It is not of material interest. However, the associated decay time, T_2^{AB} , is very often shorter than the true sample T_2 .

Internuclear interactions

Variations in local field arise from magnetic dipolar interactions between neighbouring nuclei. The interactions can either be between like nuclei (e.g. $^1\text{H} - ^1\text{H}$) or between unlike nuclei (e.g. $^1\text{H} - ^{29}\text{Si}$), though the former are generally more important for ^1H in water. These interactions give rise to true T_2 decay. The field variations are strongly time dependent due to molecular motion which serves to “average out” the interactions in “mobile” systems. This is why true T_2 relaxation is sensitive to molecular dynamics.

Electron-nuclear interactions

These are especially pertinent to cement. Magnetic dipolar interactions between nuclei, such as of ^1H and unpaired electrons on paramagnetic impurity ions such as Fe^{3+} , also contribute to T_2 decay. Since the magnetic moment of an electron is about 650 times greater than that of a hydrogen ^1H , paramagnetic relaxation is a strong effect even though the electrons are “dilute”. It should be noted that there are also very weak interactions that are magnetic in origin between nuclei mediated by molecular bonding electrons. These much smaller effects manifest as the resonant frequency shifts (chemical shift and J-coupling) that underpin NMR spectroscopy. They are not considered further here.

Magnetic susceptibility

Variations in local field can arise from spatial variations in magnetic susceptibility within the sample, due, for instance, to porosity or paramagnetic impurities. Variations in susceptibility act to distort the applied field much like a lens distorts light. Whether this is considered an intrinsic effect (contributing to T_2) or extrinsic effect (contributing to T_2^{AB}) depends very much on one's point of view. It is noted that some authors have sought to measure T_2^{AB} to characterise susceptibility variations in order to infer microstructure [29].

Whatever the cause of relaxation, the observed signal decay rate, denoted as the sum of all the intrinsic and extrinsic rates, is:

$$\frac{1}{T_2^*} = \frac{1}{T_2^{AB}} + \frac{1}{T_2} \quad (3)$$

The same nuclear–nuclear and electron–nuclear interactions that are responsible for T_2 relaxation also give rise to T_1 relaxation. However, whereas T_2 relaxation is strongly influenced by both static and dynamic aspects of the local field, T_1 relaxation is only affected by dynamic aspects. It is therefore always a slower process. For this reason also, T_1 relaxation is not influenced by magnetic field inhomogeneity, which is “static” in character.

Relaxation in liquids, pores and solids

T_2 relaxation in bulk water

In pure bulk liquids, there is rapid molecular tumbling so that the local magnetic field experienced by any one ^1H due to its near neighbours is temporally averaged to zero. All nuclei experience the same, near zero, average local field. In consequence, the T_2 relaxation rate is very slow and the relaxation time long – a few seconds for bulk water at room temperature. As molecular motion is reduced, for instance by lowering the temperature or raising the fluid viscosity, the effective local fields increase steadily. Therefore, T_2 gets shorter and shorter. These ideas are described quantitatively in the classic theory of Bloembergen, Purcell and Pound [30]. The relaxation can also be hastened by the addition of dissolved paramagnetic materials.

Relaxation in crystalline solids

Reduced molecular motion is taken to the extreme in solids. Here, T_2 relaxation is dominated by the static distribution of local inter-nuclear magnetic dipole–dipole field strengths. Relaxation is very rapid, of the order of a few microseconds. This is sufficiently fast that $T_2 \ll T_2^{AB}$ almost invariably holds true in solids. Moreover,

considering again the one-pulse FID experiment, in solids the decay cannot always be considered exponential. The distribution of local magnetic field strengths is a complicated function of the angles between the interatomic nuclear vectors and the applied magnetic field and of the nuclear separation distances. The shape of the FID decay is related to the Fourier transform of this distribution. For powdered crystals comprising pairs of static ^1H , of which calcium hydroxide (Portlandite) is a reasonable practical example, the decay is more Gaussian-like, but modulated by a distinct cosine-like oscillation. In the frequency domain it is known as a Pake doublet^[31]. More generally, for more complex molecular configurations and amorphous materials the decay is reasonably described by a Gaussian.

T_2 relaxation of water in small pores

Water in a small pore can be broadly divided into two fractions: water in a near pore surface layer, and water in the bulk of the pore, Figure 2. The water in the bulk of the pore behaves much as “free” liquid. It has a long T_2 relaxation time that is typically of the order of seconds. The water in the near surface layer has lower mobility in general and, especially in the case of cements, interacts strongly with surface adsorbed paramagnetic impurities such as Fe^{3+} and Mn^{2+} . The relaxation time is therefore much shorter and may be as short as microseconds. One therefore might expect to see two components in the relaxation time dispersion. In sufficiently large pores, this is true, save that the bulk water fraction totally dominates the surface layer fraction. However, in small pores this is generally not the case. Diffusion ensures that there is rapid exchange of the bulk and surface layer water molecules on the timescale of the relaxation. Therefore, a single averaged relaxation rate is observed for all the water. For T_2 in a saturated pore^[32, 11, 33]:

$$\frac{1}{T_2^{obs}} = \frac{\lambda S}{V} \frac{1}{T_2^{surf}} + \frac{(V - \lambda S)}{V} \frac{1}{T_2^{bulk}} \quad (4)$$

where S is the surface area of a pore of volume V , λ is the thickness of the surface layer (normally assumed to be a molecular monolayer) and T_2^{obs} , T_2^{surf} and T_2^{bulk} are the observed, surface and bulk relaxation times respectively. Normally, $V \gg \lambda S$ and $\lambda S / V \gg T_2^{surf} / T_2^{bulk}$ so that:

$$\frac{1}{T_2^{obs}} \approx \frac{\lambda S}{V} \frac{1}{T_2^{surf}} + \frac{1}{T_2^{bulk}} \approx \frac{\lambda S}{V} \frac{1}{T_2^{surf}} \quad (5)$$

For a spherical pore of radius a , $S = 4\pi a^2$ and $V = 4/3 \pi a^3$, so that:

$$1/T_2^{obs} = 3\lambda / a T_2^{surf} \quad (6)$$

The equivalent result for a planar pore of thickness b , that is often seen as a model for a cement gel pore, is:

$$1/T_2^{obs} = 2\lambda / bT_2^{surf} \quad (7).$$

The observed relaxation time is therefore a measure of the pore size. Corresponding equations exist for T_1 relaxation of water in pores.

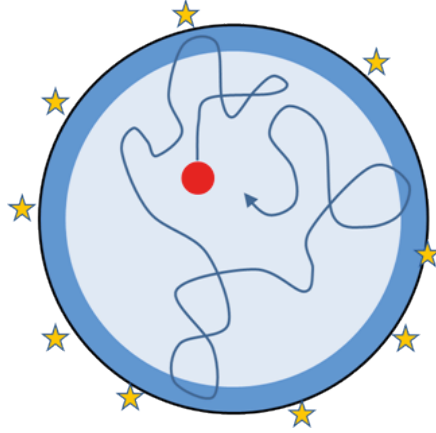


Figure 2: A water molecule (red) diffuses randomly in a pore of radius a . While in the bulk water interior (light blue) it relaxes slowly. When it approaches the surface (dark blue layer thickness λ) it relaxes more quickly, due to, for instance, the effects of surface paramagnetics (gold stars). Given fast exchange between the two regions, the observed relaxation rate is the average of the two, weighted by the time spent in the two regions, that is by the ratio of the surface layer volume ($4\pi a^2 \lambda$) to bulk volume ($4/3 \pi a^3$). The observed rate, $1/T_2^{obs} = 3\lambda / aT_2^{surf}$, is therefore a measure of pore size.

Differences between T_1 and T_2

The temporal variations in local magnetic field that lead to relaxation are properly described by a spectral density function. The primary difference between T_2 and T_1 relaxation is that T_2 is dependent on the low frequency and high frequency parts of this function whereas T_1 depends on the high frequency part only. Consequently, T_1 goes through a minimum as motion declines whereas T_2 decreases monotonically. Therefore, it can be difficult to distinguish free liquids from solids on the basis of T_1 as both have long relaxation times. On the other hand it is easy with T_2 since solids have short relaxation times whereas the relaxation times of liquids are long.

Improved experiments to measure T_2 and T_1 relaxation

Spin or Hahn echoes

The effects of variations in applied field and dipolar interactions on relaxation can be separated using spin echoes. Whereas the FID results from a single pulse, an echo results from a sequence of two pulses ^[34]. A schematic of the most common experimental variant is shown in Figure 3. The sequence comprises a 90° pulse followed at a time, τ , by a 180° pulse. The 180° pulse is of either twice the amplitude or twice the duration compared to the 90° pulse and so rotates the magnetisation through 180° . The first pulse rotates the magnetisation into the x - y plane. In the subsequent time interval, τ , the individual nuclei precess and dephase in this plane. The second pulse rotates the de-phasing nuclei 180° and so reverses their precession angle in the x - y plane. After the second pulse, the nuclei continue to rotate about local magnetic field inhomogeneities *in the same direction* so that, at time 2τ , the de-phasing characterised by T_2^{AB} is completely reversed, and the nuclei are all aligned once more in the x - y plane. The signal is recovered in the form of an echo at time 2τ . The echo looks like two FIDs back-to-back, since, after it forms, the nuclei start to de-phase once again. It is as if a gun is fired half way through the Olympic 100 m final and all the athletes turn around by 180° and head back to the start. If they continue to run at the same speed, then they all get back to the start at the same time and then run through the start as if beginning a new race in the opposite direction. However, any dephasing due to inter-nuclear interactions is not recovered. The echo is attenuated by a factor $\exp(-2\tau/T_2)$ with respect to the original FID signal. Pursuing the Olympic analogy, the athletes might interact and disrupt each other and so arrive back at the start at slightly different times. In this way, signal attenuation due to internal and external causes is separated. This description of echo formation is based on the vector model of NMR and is elaborated in Appendix A.

CPMG

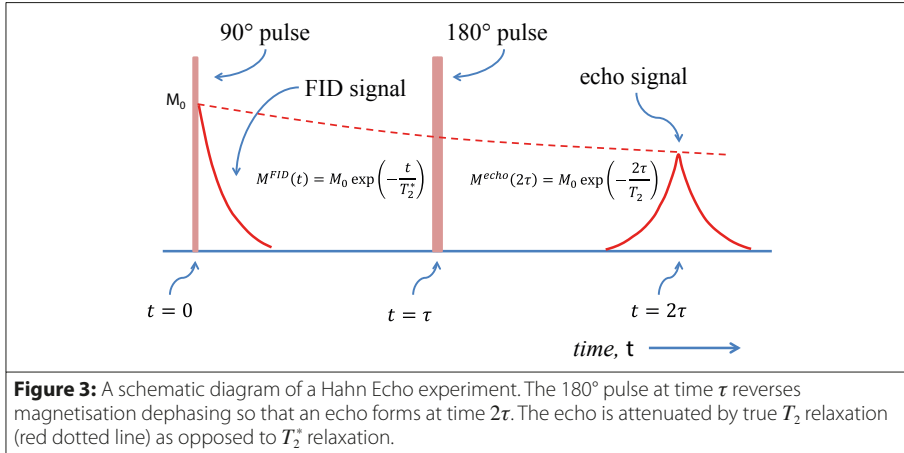
The idea of echo formation is taken further in the Carr-Purcell-Meiboom-Gill (CPMG) experiment ^[35, 36], which is used to separate evaporable water in different structural environments in cement. In this experiment, following the initial 90° pulse, a train of 180° refocusing pulses is used to generate a train of echoes from which the relaxation time T_2 can be measured in a “single shot”, as shown in Figure 4. The refocusing pulses are applied at times $\tau, 3\tau, 5\tau \dots$ and echoes are seen at times $2\tau, 4\tau, 6\tau \dots$. Since this can lead to very many pulses being applied in quick succession to span a very broad range of T_2 times (as in cements), it is possible to space the pulses and echoes logarithmically.

Saturation and inversion recovery

There are two standard methods to measure T_1 : saturation-recovery and inversion-recovery. The first method, saturation-recovery (Figure 5) involves applying a string of radio frequency pulses designed to destroy the nuclear magnetisation. Then, after a delay, τ_{sat} , a single 90° pulse is applied. This pulse yields a free induction decay the intensity of which is a measure of the recovered magnetisation. The experiment is repeated for different values of τ_{sat} in order to build the full recovery curve that is given by:

$$M(\tau_{sat}) = M_0 \left[1 - \exp\left(-\tau_{sat}/T_1\right) \right] \quad (8)$$

where M_0 is the magnitude of the equilibrium magnetisation along the z -axis and $M(\tau_{sat})$ is the value at time τ_{sat} after the initial string of pulses.



The second method, inversion-recovery (Figure 6) replaces the initial string of 90° pulses with a single 180° pulse which inverts the magnetisation. Hence, rather than seeing M_z recover from 0 towards $+M_0$, it is seen to recover from $-M_0$ to $+M_0$ so that:

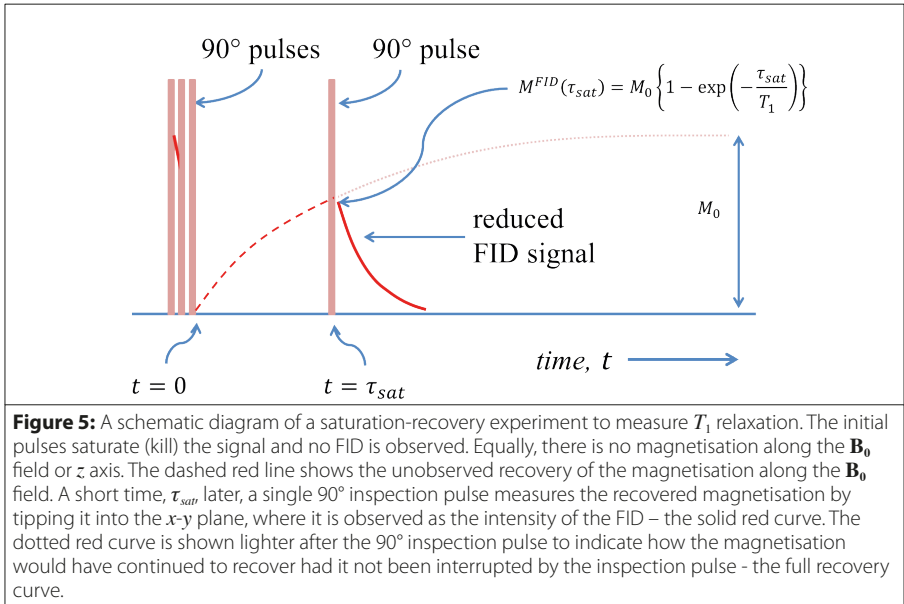
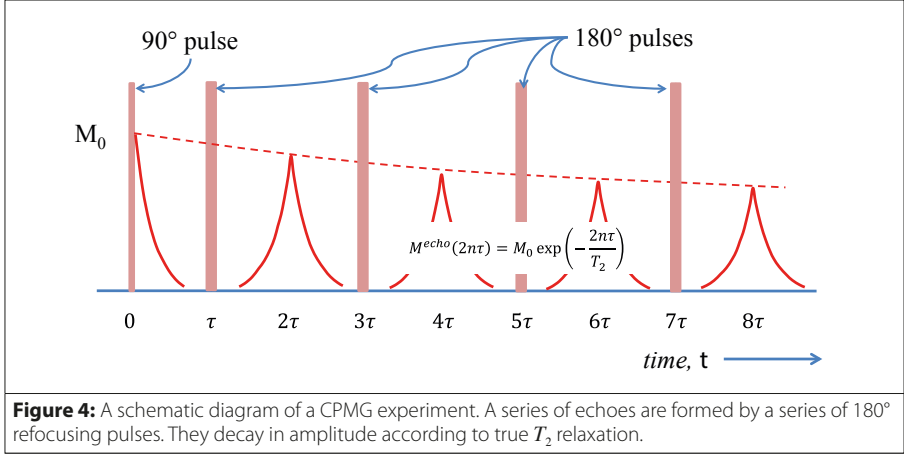
$$M(\tau_{inv}) = M_0 \left[1 - 2 \exp\left(-\tau_{inv}/T_1\right) \right] \quad (9)$$

Inversion-recovery offers twice the sensitivity of saturation-recovery. However, this advantage comes at the cost of needing to allow sufficient time between repeat applications of the sequence to ensure that the magnetisation is fully recovered before the next experiment start, and hence the recovery always starts from $-M_0$. Of course, it is possible that the initial saturation is incomplete in the saturation-recovery

experiment or the inversion is imperfect in the inversion-recovery experiment. In such cases the data are fitted to:

$$M(\tau_{sat/inv}) = M_0[1 - \alpha \exp(-\tau_{sat/inv}/T_1)] \quad (10)$$

where α is a constant.



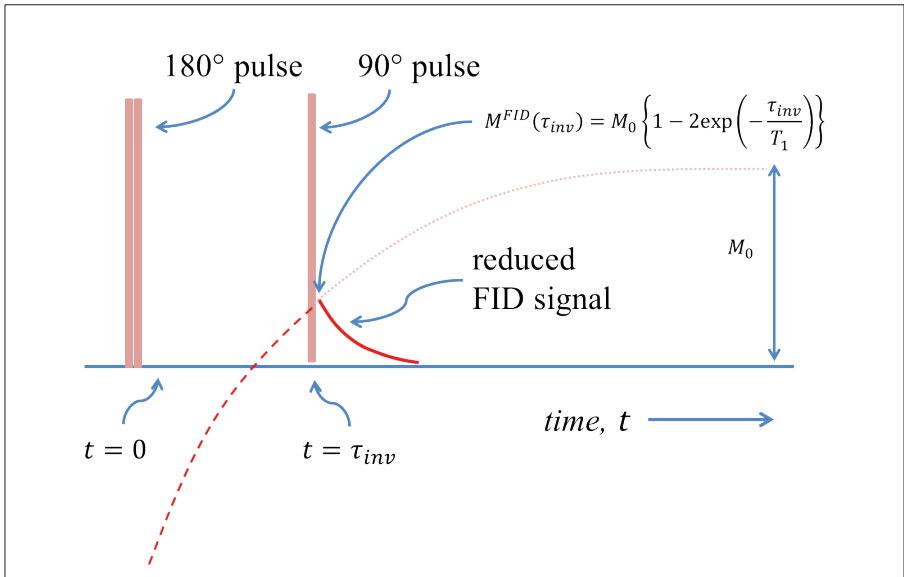


Figure 6: A schematic diagram of an inversion recovery experiment to measure T_1 relaxation. The initial 180° pulse inverts the magnetisation along $\mathbf{B}_0$ field or z -axis. No signal is seen as there is no magnetisation in the xy plane. The dashed red line shows the unobserved recovery of the magnetisation along $\mathbf{B}_0$. A short time, τ_{inv} , later, a 90° inspection pulse measures the recovered magnetisation. Note that if the wait is sufficiently short, then the observed signal is negative. The dotted red curve is shown lighter after the 90° inspection pulse to indicate how the magnetisation would have continued to recover had it not been interrupted by the inspection pulse - the full recovery curve.

A final difficulty in measuring T_1 compared to T_2 is that it is critically important to have a good measure of the equilibrium magnetisation measured at long recovery times in order to fit well the data to an exponential recovery. For a T_2 analysis, a decay is measured towards a known zero equilibrium and this is not a problem. For T_1 , the maximum value of $\tau_{sat/inv}$ must be several times, ideally at least five times, the maximum T_1 of any nuclei in the sample. Not only does this make the experiment relatively slow compared to CPMG for T_2 , it also means that a “trial” experiment must be performed in order to estimate T_1 before it can be measured!

Other methods are known for rapid, “single-shot” measurement of T_1 , but these are not widely used and are not thought suitable for cements where high quality data are required to identify well all the different components.

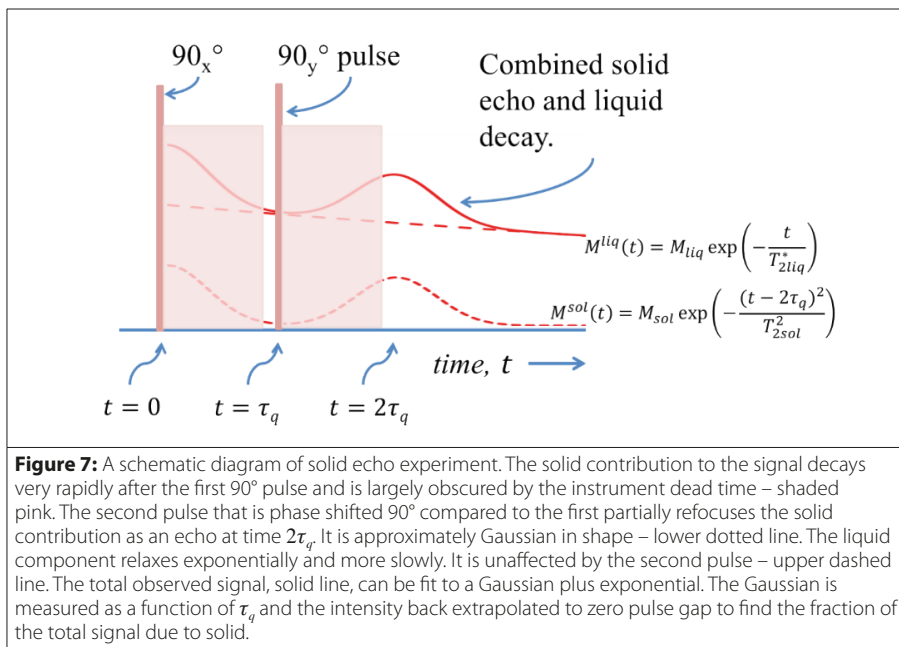
Why is it better to measure T_2 rather than T_1 in cements?

- ^1H T_2 decreases monotonically from a large value (several seconds) for bulk water through progressively smaller values for water in ever smaller pores to a very short value (microseconds) for ^1H in solids. This makes differentiation of water in different microstructural environments easy. On the other hand, T_1 is long for both water in large pores and in solids leading to potential ambiguity.
- The CPMG experiment for T_2 is a quick “one-shot” measurement for the mobile water. This compares with inversion- or saturation-recovery measurements for T_1 , either of which requires multiple “shots”. Even allowing for the fact that a “multi-shot” solid echo experiment is additionally required for T_2 in solids if wanted in addition to the mobile water analysis, the T_2 experiment is still much the faster for comparable data volumes and signal to noise ratio.
- The CPMG baseline for T_2 is known to be zero whereas the inversion or saturation recovery “baseline” for T_1 is non-zero and must be measured very carefully for accurate quantitative analysis. Moreover, average for average, the T_1 baseline measurement is the most time consuming part of the experiment!
- Notwithstanding that the solid T_1 is long, apparatus able to measure a short FID signal is still required to observe the solid signal: there is no equipment advantage in measuring T_1 compared with T_2 .

Solid echoes

Solid echo experiments, sometimes called quadrature or quad echo experiments in some cements literature, are used to quantify the amount of water in crystalline solids such as calcium hydroxide or ettringite in cements. The T_2 relaxation of ^1H in these solids is extremely fast, of the order of a few microseconds, due to the strong magnetic interactions between ^1H nuclei that are not averaged to zero by molecular motion. All spectrometers suffer a short dead-time following an excitation pulse during which no signal can be observed. It arises because the receiver pre-amplifiers are saturated by the pulse and need time to recover. In most bench top spectrometers the dead time is several microseconds and so a significant fraction of the part of the FID due to the crystalline solids cannot be seen. The solid echo pulse sequence comprises two 90° pulses differing in phase by 90° and separated by a pulse gap, τ_q . This sequence has the special property of completely refocusing magnetic dipolar interactions between rigidly bound pairs of ^1H nuclei and substantially refocusing interactions between larger groups of nuclei in more complex configurations.

A solid echo forms at time $2\tau_q$. The sequence is shown schematically in Figure 7.



The shape of the solid signal decay and hence of the echo is non-exponential. For a sample made up of pairs of ^1H nuclei, of which calcium hydroxide is actually a very good approximation, the decay shape can be calculated explicitly. The shape is reasonably approximated by a Gaussian modulated by a cosine curve. The distinctive wiggle that this creates in the decay is known as a Pake doublet. More commonly, however, the samples comprise many ^1H atoms in variable configurations. In such cases the wiggle is smoothed out and a simple Gaussian is an adequate approximation.

Most samples, of course comprise a mixture of solid and liquid. A useful property of the solid echo sequence is that the second pulse has no effect on the liquid FID so long as τ_q is short compared to both T_2 and T_2^* . This condition is generally fulfilled. Hence the composite signal after the second pulse comprises a Gaussian solid echo of width of a few microseconds centred on time $2\tau_q$ after the first pulse and an approximately exponential decay with time constant T_2^* (potentially milliseconds) with time origin at the first pulse. In order to account for the decay of the solid echo intensity due to imperfect refocusing of the solid signal, the echo can be measured as a function of τ_q and the echo intensity back-extrapolated to zero pulse gap in order to measure the true solid signal fraction. Back-extrapolation is made using a second Gaussian, on the basis of work by Powles and Strange^[37] and by Boden and

co-workers^[38, 39]. The echo intensity thus depends on τ_q as:

$$M_{sol}(\tau_q) = M_{sol}^0 \exp\left(-\frac{\tau_q^2}{T_{2sol}^2}\right) \quad (11)$$

where T_{2sol} is a measure of the (non-exponential) solid decay time and M_{sol}^0 is the value of M_{sol} at $\tau_q = 0$. In practice, given finite pulse lengths, it is generally better to back extrapolate to actual zero gap between the pulses, that is to replace τ_q on the right hand side of equation 11 with $\tau_q - t_{pg0}$.

Imaging

Magnetic resonance imaging enables magnetic resonance parameters to be spatially mapped. Data can be acquired in one dimension, in which case it is usually termed profiling, or in two or three dimensions. Most commonly imaging refers to mapping a two-dimensional slice within a three-dimensional object. Spatially resolved magnet resonance acquires an NMR signal from a localised region within a larger sample. For cements, the most common parameters that are mapped are water concentration weighted by T_1 and/or T_2 relaxation, although the subject remains in its infancy.

Spatial encoding

Magnetic resonance imaging relies on the application of a magnetic field gradient, $\mathbf{g} = \nabla \mathbf{B}_0$ to disperse the resonance frequencies of nuclei with spatial position, $\mathbf{r}$. A practical and useful form of one dimensional imaging (*profiling*) known as frequency encoding with T_2 weighting is shown in Figure 8. The figure shows an echo experiment analogous to Figure 3 except that a field gradient is applied during the first de-phasing period and again during the echo data collection. The extra precession frequency at position $\mathbf{r}$ is given by $\delta f = (\gamma/2\pi)\mathbf{g} \cdot \mathbf{r}$ so that the echo signal is described by:

$$S(t') = \int_{\mathbf{r}} \rho(r) \exp\left(-2\tau/T_2(r)\right) \exp(j\gamma \mathbf{g} \cdot \mathbf{r} t') d\mathbf{r} \quad (12)$$

where $\rho(r)$ is the ^1H concentration at location $\mathbf{r}$ (*i.e.* the profile of the sample) and t' is the time measured from the echo centre ($t' = t - 2\tau$). A one-dimensional profile of the sample, weighted by the $T_2(r)$ attenuation factor, is generated by Fourier transformation of the signal data with respect to time. Multi-dimensional imaging is achieved by combinations of *frequency* and *phase* encoding and of *slice* selection in different directions. Phase encoding measures the echo as a function of $\mathbf{g}$ rather than t' while slice selection applies a shaped excitation pulse in the presence of the gradient. Multi-dimensional imaging requires gradient pulses in orthogonal directions and 2 or 3 dimensional Fourier transforms.

The NMR phase cycle

An important aspect of all the NMR experiments described in this section is the so called pulse phase cycle.

The phase cycle refers to the radio frequency phase (x' , y' , $-x'$ or $-y'$) of one pulse compared to the next and to the phase of the reference signal in the signal detector. The phases can vary both within a sequence and also between one running of the sequence and the next. Hence, an experiment is normally run for several different combinations of pulse phases within a cycle and the results averaged together. The purpose of the phase cycle is:

- To cause nuclei to rotate about different axes. In consequence and for example, if the phase of the 180° refocusing pulse of a Hahn echo experiment is shifted by 90° compared to the first 90° excitation pulse, then the echo forms as shown. However, if the phase is not shifted, then the echo appears negative. Indeed, without the phase shift, alternate echoes of a CPMG train appear with alternate sign, positive and negative.
- To correct for systematic errors. For instance, alternating the phase of refocusing pulses within a CPMG sequence $\pm 90^\circ$ with respect to the first pulse can correct for slight rotation angle imperfections.
- To refocus relaxation for specific interactions while leaving others unaffected. This is exploited in the solid echo experiment, where the phase shift is required to refocus inter-nuclear dipolar interactions between nuclei in solids while leaving nuclei in liquids unaffected.
- To remove unwanted signals. In the stimulated echo experiment used in diffusion measurements, the average of at least two experiments with different phase cycles is required to ensure that only the wanted “stored” signal is measured and that unwanted signals that otherwise “feed-through” are averaged to zero.
- To correct for baseline offsets and receiver channel gain imbalances. For instance, measuring the FID for a combination of four different pulse phases can eliminate mismatch between the gain of the real and imaginary signal channels and also eliminate a baseline offset in either channel.

It is important to get the phase cycle “right” for any given experiment. Without specialist knowledge, it is therefore usually best to use the sequence provided by the instrument manufacturer. Phase cycles are normally a sequence of four or eight variants. For this reason it is good practice to restrict the number of averages in an NMR experiment to a power of 2 greater than 4 so that the sequence is always run through complete cycles.

Image contrast

Equation 12 assumes that the echo is uniformly decayed over the sampled region of data by a factor $\exp(-2\tau/T_2(r))$, that is $2\tau \gg |r'|$. The profile intensity is therefore weighted by a factor dependent on $T_2(r)$ so that for equal density, long T_2 components show brightest in the profile. T_1 weighted profiles can be generated by several means, including by placing saturation pulses ahead of the sequence akin to saturation-recovery. In this case, short T_1 components show brightest.

Image Resolution

If the echo is sampled at N points spaced at t_d intervals then the image pixel size and field of view (FOV) are given by:

$$\delta r = (2\pi/\gamma) \cdot (1/gNt_d) \text{ and } r^{FOV} = N\delta r \quad (13)$$

respectively. Stronger gradients and longer sampling intervals improve the resolution. However, for a given gradient strength, the true image resolution, as opposed to pixel size, is ultimately limited by T_2 . In the absence of molecular diffusion, the limit is given approximately by:

$$\delta r_{best} = (2\pi/\gamma) \cdot (1/g\pi T_2) \quad (14)$$

so that increasing t_d without limit is not an option to improve resolution. Increasing the gradient strength without limit is not necessarily an option, either, for even better resolution. For liquid systems with molecular diffusion, as g increases, so the effective T_2^{eff} decreases as explained in the next section. An excellent text covering all of these concepts is provided by Callaghan^[40].

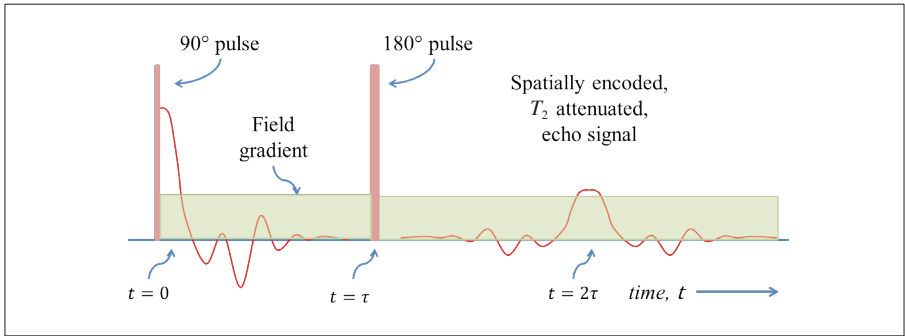


Figure 8: A schematic of a Hahn spin echo sequence with additional frequency encoding gradient pulses (green) for 1D imaging. The Fourier transform of the echo signal is a T_2 weighted profile of the sample.

Diffusion analysis and q -space imaging

A pair of magnetic field gradient pulses applied as in Figure 9 may be used to measure molecular diffusion. This is the pulsed gradient spin echo experiment. The first gradient pulse of length δ and strength g encodes each nucleus with a phase rotation angle in the transverse plane dependent on its position at the time of the pulse. If the nucleus does not move, the second pulse completely “unwinds” this rotation and the echo appears as normal. If the nucleus moves in the interval Δ (the time from one gradient pulse to the next), then a residual phase angle is left. Averaged over very many diffusing nuclei, the echo signal is attenuated according to:

$$S(q)/S(0) = \exp\left\{-\gamma^2 g^2 \delta^2 \left(\Delta - \delta/3\right) D\right\} \sim \exp\{-q^2 \Delta D\} \quad (15)$$

where $q = \gamma g \delta$ is a wavenumber with units of reciprocal length, Δ is the “diffusion time”, and D is the diffusion coefficient. The approximate equality in equation 15 holds in the limit $\delta \ll \Delta$. The diffusion coefficient is defined by:

$$D = \frac{\langle X^2 \rangle}{6\Delta} \quad (16)$$

where $\langle X^2 \rangle$ is the mean square displacement of the diffusing nuclei in time interval Δ . A variation of this experiment, the pulsed gradient stimulated echo, replaces the 180° pulse by two 90° pulses separated by a time τ_{store} . The advantages are that the magnetisation is stored along the z -axis during this time and so undergoes only (slow) T_1 relaxation. Also, while stored, the magnetisation does not de-phase due to diffusion in background field inhomogeneities.

Measuring D as function of Δ provides a means of investigating microstructure: this is the basis of the NMR technique q -space microscopy. In essence, if Δ is sufficiently short, then nuclei in pores diffuse as if they are in a bulk liquid and the bulk liquid diffusion coefficient is measured. However, as Δ increases, the maximum diffusion distance is limited by the pore wall confinement, and so the apparent diffusion coefficient is reduced. For liquids with diffusion coefficients comparable to water (circa $2 \times 10^9 \text{ m}^2/\text{s}$), the method probes “average” structural properties on a scale of the order of micrometres. NMR q -space microscopy is described in a second excellent text by Callaghan ^[41].

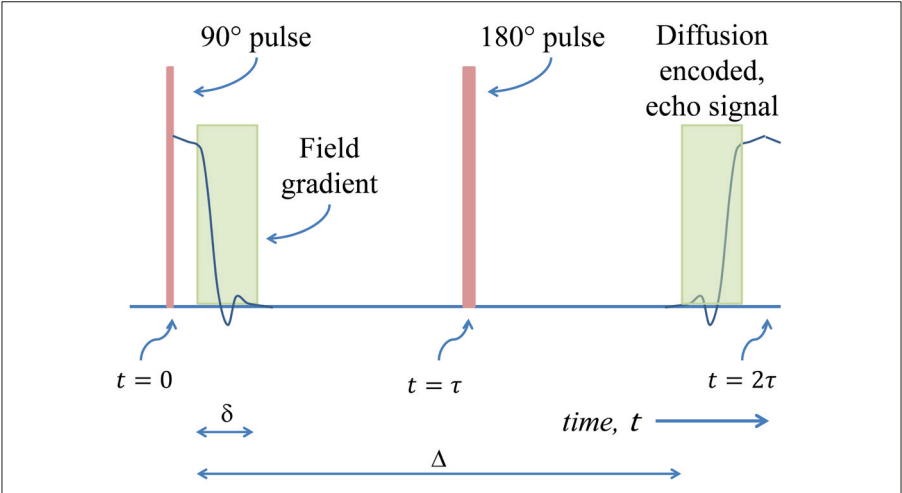


Figure 9: A schematic of a Pulsed Field Gradient experiment to measure diffusion.

Suitable equipment

- Schematic
- Bench top magnets
- Magnet requirement for cements
- Spectrometer
- Spectrometer requirements for cements
- Magnetic field gradients

Schematic

Figure 10 shows a block diagram of a benchtop NMR apparatus for measuring relaxation in materials such as cements and concretes. The principal components are the magnet and the spectrometer and probe. Optional parts include the magnet shims and field gradient coils and some auxiliary amplifiers.

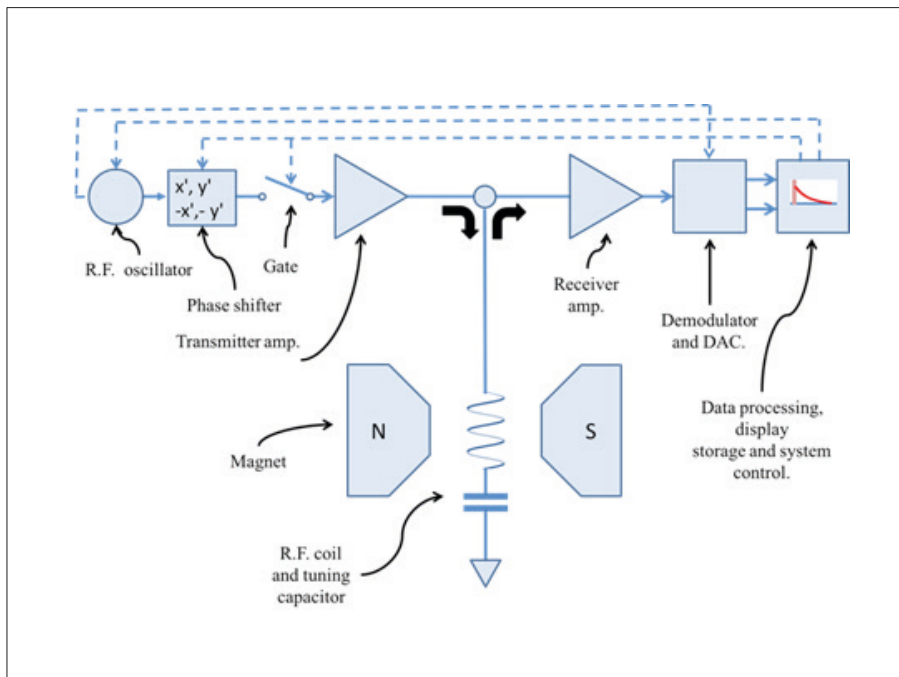


Figure 10: A schematic of an NMR spectrometer suitable for NMR relaxation experiments. The sample is placed within the R.F. coil in the homogeneous region of the magnet. Radio frequency excitation signals and NMR signals are shown by the solid blue arrows running left to right. Control and reference radio frequency signals are shown by dashed arrows. Magnetic shim and gradient coils that are sometimes provided to improve the magnetic homogeneity and to enable imaging / diffusion experiments respectively are not shown.

Bench top magnets

Most modern bench top equipment is based around a rare-earth permanent magnet made from an alloy of neodymium, iron and boron (Nd-Fe-B) that produces a homogeneous magnetic field over a central sample volume. By far the most common design comprises two circular pole pieces held in a square or C-shape steel frame or yoke that provides the return path for the magnetic field flux. With this design, the field is directed straight across between the pole pieces. The sample is placed centrally between them.

Magnetic field strength and sample volume

Permanent magnets for NMR are generally restricted to field strengths less than about 1 T. Field strengths of 0.05 to 0.5 T equivalent to NMR frequencies of 2 to 20 MHz for ^1H are common. Sample volumes are typically one to a few centimetres in diameter, with the homogeneous field volume tending to decrease as the field strength increases due to the weight of the necessary magnetic material, ease of construction and cost.

Magnetic field homogeneity

After field strength, magnets are characterised by their field homogeneity over the sample volume. To achieve good homogeneity, the pole diameter is significantly larger than the sample size. For relaxation and spectroscopy analysis, the field homogeneity is typically defined as the half-height width of the field strength distribution over the specified volume. However, for imaging applications it is better to specify instead the maximum magnetic field deviation from the mean value over this volume, since field deviation translates directly to image distortion. Either way, the homogeneity is usually specified in parts per million (ppm) over a spherical volume, or diameter of sample volume (DSV).

Care needs to be taken in as much as the absolute width of the field distribution increases as the field strength increases for a fixed homogeneity expressed in parts per million. For this reason, it is safer to specify the required homogeneity for relaxation analysis not in parts per million or even in absolute Tesla but as an equivalent NMR ^1H T_2^{AB} (see chapter 2) using the relationships:

$$1/\pi T_2^{\text{AB}} = \Delta f_0 = \gamma \Delta B_0 / 2\pi$$

Magnet shimming

Magnet homogeneity can be improved by either *passive* or *active* shimming.

Passive shimming involves carefully sticking small pieces of magnetic material to the pole pieces in order to modify the field. Finding the necessary position of these pieces requires accurate measurement of the field shape and then detailed calculation. Passive shimming is suited to the reduction of large inhomogeneities and requires specialist equipment, so is usually performed by the magnet manufacturer.

Active shimming uses steady electric currents flowing in shim coils around the active volume to modify the field profile. Active shimming allows much finer control of the homogeneity especially if multiple coils are provided. The currents in active shims can be “updated” regularly, which is useful since magnetic field homogeneity is sensitive to changes in the local magnetic environment and even the magnetic susceptibility of the sample. Active shimming requires, of course, additional current controllers. Many instruments come with “auto-shim” computer control of these currents. The shim quality should be checked regularly.

Magnetic temperature control

Additional to shimming, the magnetic strength of Nd-Fe-B is temperature sensitive. The temperature coefficient of Nd-Fe-B is of the order of -1000 ppm per °C. Many bench top magnets therefore come with temperature control and are maintained and operated a few degrees above room temperature, say at 30 °C in temperate climates.

Alternative magnet designs

There are designs of permanent magnet with homogeneous field profiles other than C-frame magnets, such as a Halbach magnet ^[42]. Halbach magnets comprise a cylindrical ring of Nd-B-Fe elements, the relative orientation of which is rotated around the ring one to the next. The end result is a compact design with a uniform magnetic field directed across the ring diameter. Halbach magnets can be relatively lightweight as a steel yoke is not required, making them potentially suitable for transportable equipment. A further advantage is that the stray magnetic field external to the device is low. However, for practical designs with a low number of elements, the homogeneity is often not as good as that for the equivalent square or C-frame design.

A variety of designs target a useful magnetic field *outside* of the device. Such magnets are used in one-sided or *in-situ* applications where the sample size greatly exceeds any reasonable magnet size. Such magnets can be put up against large structures and NMR signals obtained from the sub-surface layers. The depth of penetration of the

magnetic field into the surface generally scales with the magnet pole piece size so that a few centimetres is practical. In some designs, the objective is to achieve a region of homogeneous magnetic field within a defined region of the sample below the sample surface. In others, the objective is to achieve a controlled field gradient across a region to enable more spatially localised measurements either by varying the NMR frequency or by moving the magnet. Designs include those by Cooper and Jackson^[43] that has found application in down bore hole oil well logging, the now highly developed NMR Mouse® (Mobile Universal Surface Explorer)^[44,†], used across a broad range of materials and heritage science applications, and the Surface GARField (Gradient at Right-Angle to Field) that was specifically made for the built environment^[45].

Health and safety requirements

There are numerous potential hazards associated with working with magnets. While these are generally less severe for work with bench top permanent magnet systems than with clinical scanners or high field superconducting laboratory spectrometers they nonetheless must be fully considered.

Magnet requirements for cements

Field strength

A magnetic field strength in the range 0.2 to 0.5 T (approximate ¹H frequency 8 to 20 MHz) is required for routine analysis of cement materials. If the field strength is significantly smaller than this, then the signal to noise ratio, which varies approximately as $B_0^{1.75}$, becomes too small. On the other hand, if it is much greater, then the magnetic susceptibility inhomogeneity of the sample that spoils the field homogeneity can start to become significant. Notwithstanding, the authors have, on different occasions, obtained useful data on cements and concretes from magnets operating at as low as 0.025 T (1 MHz) and as high as 1.5 T (60 MHz).

Field homogeneity

It is authors' experience that it is necessary to have a magnet homogeneity equivalent to $T_2^{AB} = 3$ ms or better to characterise reliably cement materials using ¹H NMR. Even though a lower homogeneity magnet should, in principle, suffice for CPMG experiments, the authors find that this is not the case, probably because multiple T_2 components on a comparable timescale are being resolved. To do this, very good data quality is required, free from systematic artefacts including T_2 dependent echo shapes and spurious phase rotations.

† <http://www.nmr-mouse.de/>

Magnet temperature

A down-side of operating the magnet at a temperature significantly above room temperature for cements is that samples will warm and water will evaporate during measurement, unless separate sample temperature control is provided.

Temperature stability

A typical full cycle of experiments to fully characterise one sample may take of the order of 30 minutes. It is desirable to have the field stability at least as good as, and preferably better than, the field homogeneity, say a 100 Hz line-width. The long term magnet temperature stability needs to be of the order of 0.02 °C/h for a 0.25 T magnet. However, the thermal mass of magnets helps protect them against short-term fluctuations in temperature. One option is to run the magnet in a temperature controlled laboratory.

Sample size

The required magnet size and weight depend on the required sample DSV and field strength. A 10 mm diameter sample suffices for the study of cement pastes. However, for concretes, samples upwards of 35 mm are required, dependent on aggregate size. A typical bench top magnet meeting these specifications has a footprint of 0.25 to 0.5 m² and weighs several tens of kilograms. Notwithstanding, one-sided magnets of smaller size and weight are available that can be used to inspect small regions of much larger samples, *e.g. in-situ* applications for mortars and concretes.

Spectrometer

General aspects

The key parts of the spectrometer are identified in Figure 10. The spectrometer has four main parts: radio frequency electronics for signal excitation (transmit) and detection (receive), the probe, and the computer control system.

The radio frequency transmit side of the electronics comprises a chain of a radio frequency source, a phase shifter, a gate and a power amplifier. Typical bench top spectrometers derive a frequency reference from a temperature controlled crystal oscillator and use a mix of soft and hardware to create from it the basic sinusoidal waveform at the NMR frequency. The phase shifter enables the phase of excitation pulses to be varied one from the next under computer control. The gate is computer controlled and switches the excitation pulses on and off. The power amplifier lifts the radio frequency pulses to sufficient intensity to excite the nuclei. The amplifier

is typically rated in the 0.1 to 1 kW range for bench top applications, though more power is likely required for larger concrete samples. Often the power amplifier comes as an integral part of the spectrometer, *i.e.* in the same box. However, a separate unit is just as common.

The radio frequency receive side comprises a pre-amplifier and amplifier to amplify the signals coming from the probe, two-channel (*i.e.* real and imaginary) signal demodulators that use the original NMR frequency source as a reference to bring the signal down to baseband and two analogue-to-digital converters, one for each channel – real and imaginary. The preamplifier input is normally protected from overload by crossed diodes to ground.

For bench top equipment, the probe is typically a coil of wire wound around a glass former such that the longitudinal axis of the coil, and hence the magnetic excitation field $\mathbf{B}_1$ of the pulses, is orthogonal to the applied magnetic field, $\mathbf{B}_0$. The coil is tuned to the Larmor frequency by the addition of a series or parallel capacitor. A further parallel or series capacitor is added to match the impedance of the tuned circuit to that of the spectrometer, usually 50 Ω . The probe is connected to the transmitter and receiver circuits through a multiplexer that often comprises no more than series crossed diodes in the transmit line and an impedance converter (quarter wavelength coaxial cable or lumped LC circuit elements) leading to the receiver pre-amplifier.

A key parameter associated with the probe is the quality factor Q of the coil. This is defined as:

$$Q = 2\pi f_0 L_c / R_c \approx f_0 / \Delta f_0 \quad (17)$$

where L_c and R_c are the coil inductance and resistance respectively and where Δf_0 is the bandwidth of the tuned radio frequency coil circuit. In general, a high value of Q improves the signal to noise ratio of the experiment.

The excitation pulse length should be as short as possible. The pulse length scales with the square root of the NMR frequency and probe volume and inversely with the square root of the transmitter amplifier power and probe Q . In consequence, for a given frequency, powerful amplifiers, small probe volumes and again high Q are all good. However, the Q cannot be increased without limit. The spectrometer dead time, that is the time required for the receiver amplifiers to come into linear operation following the inevitable overload of the excitation, and hence the minimum T_2 that can be sensed, scale with the ratio Q/f_0 . Also, the pulse bandwidth, approximately equal to $1/t_{p90}$, must be commensurate with Δf_0 . This sets the maximum Q . Thus, for a given sample volume, the minimum amplifier power is determined. Note, however, that the dead time cannot be shorter than the switching (off) time of the transmit power amplifier or the recovery time of the receiver pre-amplifier.

The whole spectrometer is controlled by a computer. The computer is responsible for maintaining accurate phasing and timing of the excitation radio frequency pulses, switching between transmit and receiver mode, and storing, displaying and processing the received signal. With most modern systems signal processing normally includes digital filtering. Usually, dedicated digital control cards that can be programmed from the computer are incorporated within the spectrometer for time critical parts of these operations.

Spectrometers are normally supplied with a range of pulse sequences pre-programmed. FID, Hahn (spin) echo, CPMG (with constant pulse gaps), T_1 inversion and T_1 saturation recovery are normally amongst these. The solid echo sequence is less common as standard, but can invariably be programmed easily by modifying a spin echo sequence so as to have the two pulses made to be of equal flip angle and 90° phase difference. The CPMG sequence with logarithmically spaced echoes is generally not standard either but again can usually be created by adaption of the normal CPMG sequence. Data analysis software is also commonly provided including phase rotation, baseline subtraction, Fourier transformation, exponential fitting and in many cases inverse Laplace transformation.

Spectrometer requirements for cements

Pulse length and dead time

The most critical aspect of the spectrometer from the perspective of characterising cement pastes is the combined 90° pulse length and the receiver dead time. Good practice requires a combined time less than or equal to $\sim 15 \mu\text{s}$, but the rule is the shorter the better, and $10 - 12 \mu\text{s}$ is highly desirable in order to detect quantitatively the crystalline solids with short T_2 . For a 10 MHz system with a 10 mm probe this can typically be achieved with a fast recovery pre-amplifier, and a broadband power amplifier of a few hundred watts.

Digital electronics

Other spectrometer parameters of importance include the maximum sampling rate of the signal. The signal must be sampled many times within the FID period. Data capture rates of at least 1 MHz are normally needed for solids, much less for liquids only. Data storage capacity and maximum numbers of echoes and/or signal averages are not generally a constraint with modern machines that have effectively “limitless” memory, although this may not be the case for advanced data intensive imaging applications.

Magnetic field gradients

Magnetic resonance imaging (MRI), *i.e.* making maps of NMR parameters across a chosen planar slice of a sample, or magnetic resonance profiling, *i.e.* making a one dimensional profile across a sample, requires the addition of switched magnetic field gradient sets to the homogeneous magnet. They are used in order to generate magnetic field gradients in each of one, two or three orthogonal directions (x , y and z). The field gradients are designed around current carrying coils of conductor (copper) that are variously wire-wound on formers or etched onto printed circuit boards. The design of these coils is critical in order to ensure constant gradient strength across the sample, to minimise stray fields in magnetic pole pieces that lead to eddy currents and hence stray fields when the gradients are switched, and to generally maximise the gradient per unit current and minimise inductive switching times. The technology is well established. As with shims, gradients require additional current generators (gradient amplifiers) and pulse controllers within the spectrometer. The same coils can be used for diffusion experiments. However, if imaging and diffusion are not required, these additional items are not needed.

Specimen preparation

- Introduction
- Sample size
- Curing condition
- Samples for elevated temperature measurements
- Conductive samples

Introduction

NMR as discussed in this Guide is principally concerned with measuring the pore size distribution and the ratio of evaporable to chemically bound water of a cement based material. To that end, the most obvious point to note is that an evaporable water signal is only observed from saturated materials. The second most obvious comment is that the sample must be contained or wrapped in materials that do not contain hydrogen. Glass tubes are the most common choice and are recommended. These are generally sealed by a rubber or plastic cap well away from the sample. PTFE sample holders and PTFE tape are also sometimes used. However, care should be taken with fluorine based materials such as PTFE. The ^{19}F resonance is at a frequency only about 6% lower than ^1H . At low NMR frequency using a spectrometer with short microsecond pulses and a wide receiver bandwidth, it is quite possible to detect stray ^{19}F signals corrupting the ^1H signal. Perspex® (PMMA) and Parafilm® are both sometimes used with care. The T_2 of Perspex® is sufficiently short that it only corrupts the signal from chemically combined water. Parafilm® gives a strong signal that, even from a small wrapping of tape, may be misinterpreted as a long T_2 component. Sample holders made from metal (or any other conductor) are not appropriate for NMR.

The following sections describe observations concerning sample preparation that the authors have found can influence results and lead to apparent anomalies, if not properly considered.

Sample size

The most obvious point to note here is that the sample must be large compared to the maximum aggregate size in order that the sample measured is representative of the macroscopic material. For cement pastes, cylindrical samples of the order of 10 mm diameter and 10 mm long are widely studied in bench top equipment. If it is desired to measure samples under controlled wetting and drying conditions, then crushed mm sized pieces of paste are more appropriate as these can be wetted or dried quickly. For concretes with 8 - 16 mm aggregate, a sample diameter of 30 - 50 mm is more appropriate, while 20 - 30 mm suffices for most mortars.

A decision needs to be made as to whether a test sample is fully within the probe (defined by the region of B_1 homogeneity) or extends well beyond it. Small samples can usually be contained fully in the coil and this is generally preferred, save that a significant fraction of the sample may be external surface with non-representative properties due to, for instance, sedimentation or surface compaction. It is preferred as uniform pulse flip angles lead to better quality data with fewer systematic artefacts such as, for instance, a damped oscillation in the intensity of the first few echoes of

a CPMG echo train that can seriously hinder accurate multi-component exponential fitting.

If part of the sample extends beyond the sensor volume, then it is best that it extends well beyond it. If this is not the case, the external sample surface falls in the fringes of the region of uniform B_1 where flip angles are declining rapidly compared to in the probe centre. If this is the case, the intensity of the signal is very sensitive to the exact sample size and positioning. If the sample extends fully beyond the coil, then the advantage is, of course, that sample surface heterogeneities are not a problem and sample positioning is not so exacting.

Caution must be applied when using cut or cored samples. If cutting or coring is carried out “dry”, surface water is likely to evaporate leaving the surface unrepresentative of the bulk material. If cutting or coring is carried out “wet”, samples that are not already saturated with water are compromised. This includes all samples cured “sealed” for which chemical shrinkage leads to dry capillary voids, large samples cured underwater into which the excess water cannot always penetrate due to low permeability, and samples obtained by coring built structures.

Curing condition

Test samples are normally cured in controlled conditions: underwater and sealed curing are common choices. If cement samples are cured sealed, for instance wrapped in plastic film, then it must be realised that chemical shrinkage leaves a significant fraction of the capillary porosity devoid of water. The total water content of the sample is known accurately, but the total pore volume is poorly specified, which is an issue if the measurement targets hydrate density. If samples are cured underwater, there is reasonable expectation that capillary forces will draw additional water into chemical shrinkage voids as the sample cures so that, in principle, the total porosity is accessible. However, due to the rapidly decreasing permeability with degree of hydration, this process is not as effective as might be thought, and the capillary porosity at the centre of even a 10 mm sample can remain unsaturated. Chen *et al.* ^[46] have published data on this effect. The solution is to crush the sample early during hydration so as to have small, millimetre-sized pieces. For the same reason, the excess water required for underwater curing has to be administered to the sample very early during hydration. Colleagues of the present authors have on occasion adopted the procedure of adding a thin layer of water above pastes as little as 1 hour after mixing.

A further consideration is sample storage after initial curing. If samples are not stored at very high humidity, then larger full pores will empty according to the Kelvin equation:

$$\log\left(\frac{P}{P_0}\right) = -\frac{2\sigma V_w}{r_c R_G \vartheta} \quad (18)$$

Where:

P and P_0 are the actual and saturated water vapour pressure

σ is the surface tension

V_w is the molar volume of water

R_G is the gas constant

ϑ is temperature

r_c is the maximum size of a pore in which liquid water will condense

According to this equation, spherical pores of 0.1 μm in size will empty at a relative humidity of about 99% meaning that water vapour is rarely able to condense into larger pores.

It is for reasons of sample pores “drying” that many NMR experiments report very small capillary porosity fractions. Steps may be taken to fully saturate samples. However, Muller ^[47] has reported that even “vacuum saturation” may not be sufficient for centimetre-sized samples. Data on isopropanol exchange by Kowalczyk *et al.* ^[18] leads to a similar conclusion.

There is also the problem of leaching for underwater cured samples: ions diffusing out of the sample and into the excess water. For this reason, it is normal to use a liquid that mimics the “pore solution”. Saturated calcium hydroxide solution is a common choice.

Nanocem, in the context of European Marie Curie Training Networks funded by the European Community, has developed a series of guidelines, summarised for cements in ^[4, 47], that suggest precise means to mix and prepare cement materials in order to achieve reproducible results from laboratory to laboratory.

¹www.nanocem.org

Samples for elevated temperature measurements

The main issue with making measurements at elevated temperature is that samples are normally placed in NMR tubes. When the sample temperature is raised, some of the capillary water evaporates. As a result, there is loss of control and possibly variation of the sample water content during the measurement. Worse, some of the water that evaporates usually condenses above the sample on the glass walls of the NMR tube. If it is anywhere near the sample, and it invariably is, this water is detected in the experiment as a poorly characterised signal, leading to error. Solutions generally involve connecting a cold-trap to the sample tube and/or filling the free sample volume in the tube with a very closely fitting glass rod.

Conductive samples

Due to the pore water, saturated cements and concretes can be weakly conducting. Conductive samples can lead to inductive losses of the radio frequency irradiation, skin depth effects and heating. This is not normally a problem for NMR analysis of, *e.g.* white cements, but can be significant problem for, *e.g.* slag concretes.

Data recording and analysis

- Setting up the spectrometer
- Using CPMG to measure gel and pore water in cement
- Combining the solid echo and CPMG data

Setting up the spectrometer

Before quantitative measurements can be started, it is necessary to set up the spectrometer. This is best done initially using a sample of water doped with a small amount of, e.g. MnCl_2 , to shorten the T_1 relaxation time to a few hundred milliseconds and hence speed the process. A concentration 10 to 100 μM usually suffices. However, it is often necessary to fine-tune the parameters using a cement sample afterwards due to the effects of differing sample size, magnetic susceptibility and relaxation times. The parameters to be set include: the resonant frequency; the magnet shim, the P_{90} and P_{180} pulse lengths (or intensities); the receiver gain; the receiver phase; the data sampling rate; filter width; number of acquisition points; the repetition delay; and the number of averages.

Getting started

Before anything else, for magnets that run above room temperature, ensure that the magnet temperature has stabilised. This might take up to 24 hours. Once the temperature and the magnetic field are stable, experimental set-up can begin in earnest. For a new machine, it may take upwards of an hour. For a known machine, the process can often be completed in minutes.

First, the set-up sample is placed in the magnet. For many instruments, this is a sample of water doped with paramagnetic ions. If the instrument has a facility to *tune the probe* – that is to tweak the capacitors of the in-built probe LC circuit so as to set its resonant frequency and match its impedance to that of the spectrometer – then this should be done now in accordance with the manufacturer's instructions. However, this facility is not common on bench top equipment; it is more often associated with high frequency spectrometers for chemical analysis.

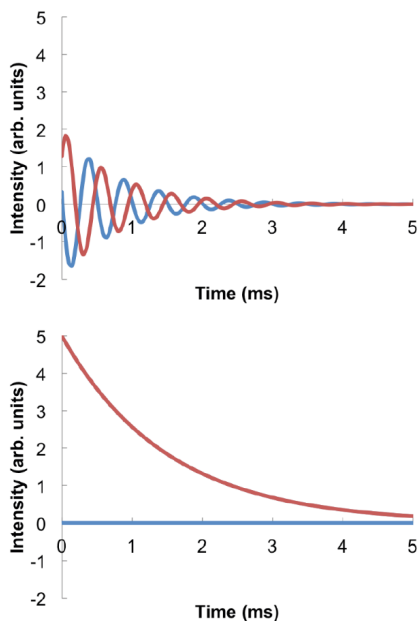
From here a simple *1-Pulse* or *FID* experiment is chosen. On most machines, there is a “most recent” or “default” parameter set that serves as a good starting point. Load these parameters and run the experiment. With luck, the real and imaginary components of an NMR signal decay will be seen on the machine display. They will probably look something like the top figure in the box opposite. The sinusoidal oscillation is because the spectrometer is *off-resonance*; that is f_0 is set wrongly. If there is an *auto set-up* routine available to set the resonant frequency, then it is a good idea to use it.

Setting the frequency

A simple means to set the frequency is to Fourier Transform the FID signal using the spectrometer in-built processing function and observe by how much the frequency is off resonance, *i.e.* the shift of the peak from resonance. Change f_0 by this amount and try again. After one or two iterations one should observe a signal that reasonably approximates to an exponential decay.

What to expect!

The top plot shows the FID as it might appear for a doped water test sample immediately after placing the sample in the spectrometer when the frequency is off-resonance. The red line shows the *real* or *in-phase* channel, the blue line the *imaginary* channel. The lower graph shows the result of correctly following the set-up procedures described in the text. The real signal has greater amplitude (the timing parameters are optimised); it looks approximately like an exponential decay rather than a sine wave (it is *on-resonance*); it extends for a much longer time (the magnet shims are optimised); and finally, all of the signal is in the real channel, and the imaginary channel is zero (*the receiver phase is set correctly*).



What can go wrong in setting f_0

In order that the Fourier transform of the FID signal correctly reveals the frequency offset, then, due to the Nyquist theorem, the actual offset must be less than half of the data sampling rate, $f_s = 1/t_d$, where t_d is the sampling period or dwell time. If this condition is not met the data appear aliased, meaning that the apparent frequency offset is wrong by an integer multiple of f_s . To avoid aliasing, it is good practice to start tuning the spectrometer with a fast sampling rate of the order of 0.1 to 1 MHz.

If the FID contains insufficient data points to reasonably see all the signal decay, then the Fourier transform will be artificially broadened making it difficult to resolve the centre of the resonance and accurately set the frequency. Using 1024 data points is usually a good place to start. 1024 is chosen as many Fourier transform routines are optimised to work with an input data size equivalent to a power of two.

As the NMR frequency is set closer to the resonant condition, so the sampling period can be increased in order to get finer control while keeping the number of points constant at a manageable level.

Setting the pulse length

Most spectrometers have an in-built function to perform this task. If not, or if the default value is far from optimum, then it must be done manually. Record signals for a range of pulse lengths starting from very short and increasing by modest intervals. The signal intensity should increase, reach a maximum and then decrease again. If all is working well, then the intensity follows a sine curve, the first maximum of which corresponds to the P_{90} condition, and the first zero crossing after the maximum to the P_{180} condition.

Some spectrometers offer the opportunity to vary the pulse amplitude rather than the pulse length. If this is the case, then the P_{90} amplitude is expected to be *circa* 6 dB less than the P_{180} amplitude. The advantage of changing the amplitude is that the pulse bandwidth (roughly equal to the inverse length) is the same for both types of pulse. This is particularly relevant to experiments performed in very inhomogeneous fields such as with one-sided magnets. On the other hand, for experiments such as solid echo, where only P_{90} pulses are required, the length is not as short as it could be if the same P_{90} is used across all experiments. This means that the combined pulse length and dead time is increased – a significant loss in this experiment in particular.

A further point to note is that some instruments default to show magnitude data. If this is the case, the data plot follows a modulus sine curve rather than a true sine curve. The P_{180} zero signal condition may not be obvious. Finally, some instruments automatically set the P_{180} as twice the length or amplitude of the P_{90} . Usually, it is better to override this feature, since finite pulse rise and fall times mean that the P_{90}

and P_{180} are rarely exactly a factor of 2 apart. It is better to set them individually and then cross-check that they are approximately as expected.

Setting the repetition delay

Once again, many instruments have an in-built function for this, but if not it must be done manually. The best procedure is to measure T_1 using a proper saturation- or inversion-recovery pulse sequence. The expected dependence of the FID amplitude on the saturation- or inversion-recovery delay, $\tau_{sat/inv}$ is:

$$M(\tau_{sat/inv}) = M_0[1 - \alpha \exp(-\tau_{sat/inv}/T_1)]$$

A basic fit to the data is used to find T_1 (or its longest component in a complex sample) and then set the repetition delay τ_{RD} at approximately five times this value, although three times will often suffice for faster data acquisition with a slight loss of quantitative accuracy in subsequent experiments. Short-cut experiments, such as rapidly averaging an FID to estimate how quickly it recovers can be used with care.

Setting the number of points, sampling rate (dwell time), and filter width

This is straightforward in as much as it is usual to record between 128 and 4096 data points in an FID. A power of 2 is chosen since this is preferred, even required, by many Fourier transformation algorithms. The sampling or “dwell” time is then simply set as a convenient FID length divided by the number of points. For bulk liquids, the dwell time is generally of the order of tens to hundreds of microseconds. For components with a short T_2 it is set to $\sim 1 \mu\text{s}$. The filter width is often calculated directly from the dwell time. Otherwise, setting the filter width to approximately the reciprocal of the dwell time is a good start. If the filter width is left unduly broad, the signal will contain more noise than necessary. If it is made too narrow, the signal will be over-smoothed.

Setting the receiver gain

The objective here is to increase the receiver gain as much as possible without saturating the receiver amplifiers and thus without *clipping* the signal. It is generally best to record different experiments on different samples with the same gain setting. This allows quantitative comparison without fear of complications from a non-linear receiver gain. Care therefore needs to be taken to ensure that the gain is set with allowance for the most signal intensive sample. On the other hand, if the gain is set too low, then digital resolution is lost for subsequent analysis. Also, the contribution of instrument noise associated with later stages of amplification unwittingly decreases the optimum signal to noise ratio of the experiment. Many instruments

offer access to the receiver phase, in which case the phase is rotated such that the initial FID signal is a maximum in the real channel and zero in the imaginary channel. If access to the phase is not offered, then the data can be phase rotated in post-processing.

Setting the number of averages

The number of averages or *scans*, n_s , is the last parameter considered here. The value chosen depends of course on the desired signal to noise ratio (SNR) of the experimental data. The SNR increases with $\sqrt{n_s}$. Generally, however, n_s needs to be an integer multiple of the number of pulse phase permutations in the pulse sequence phase cycle. The phase cycle is buried in the pulse sequence definition although sometimes the operator is given access to it. Whichever, the cycle is almost certainly 4, 8 or possibly 16 permutations long. Therefore, setting the number of averages to a power of 2 such as 128, 256 or 512 is a safe option for measurements of cement samples. For shimming the magnet with a liquid sample, as described next, four averages is likely to be sufficient. If access to the phase cycle is offered, it is generally best for the inexperienced user to accept the default phase settings.

Shimming the magnet

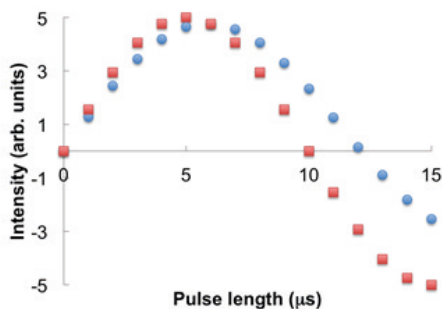
This can only be performed if the instrument has active shims or, as an alternate, gradients that can substitute as simple active shims. Again, there is often an in-built function to perform the task but unlike in other cases, it does normally require the starting point to be quite close to the optimum values to work well.

Shimming generally works best slightly off resonance, so deliberately offset the frequency by 100 - 10,000 Hz depending on T_2^* . The FID should look like several tens of periods of a decaying sine wave. Working off resonance means that the wiggles and bumps that distort the FID shape are easily visualised. Also, it is best if the pulse length is set a little less than P_{90} . This avoids complications associated with pulse inhomogeneity and mis-set length interfering with the shim. Also, the shorter pulse allows the repetition time to be reduced a little, thereby speeding the process. The objective is to systematically vary the shim currents in the coils so as to produce the signal with the longest possible decay time, T_2^* .

The long decay time is often best observed as the maximum intensity / minimum width of the signal in the frequency domain, *i.e.* after the signal is Fourier transformed. Sufficient FID data points must be collected with sufficient acquisition rate so as to ensure that the spectral peak is well resolved. Manual shimming is a black-art that is largely perfected only with practice. Knowledge and experience of the specific magnet is also useful. A T_2^* in excess of 3 ms is considered a minimum shim requirement for good measurements of cement.

What can go wrong setting P_{90} and P_{180}

It is important to ensure that the repetition delay between repeats of the experiment either for signal averaging or for checking that the pulse length is long compared to about 3 - 5 times the sample T_1 . Of course, at this stage, the sample T_1 may not be known, in which case there is a chicken and egg situation that can only be resolved by iterative experiments. For a pure water sample, $T_1 \approx 3$ s, so a repetition time of 10 s usually suffices. Doped water has a shorter T_1 and the procedure can be conducted more quickly. If the condition for repetition time is not met, the magnetisation does not fully recover between experiments, and a reduced maximum intensity will be found for a pulse length somewhat shorter than required for a true P_{90} .



The red data points show the ideal dependence of the signal amplitude on pulse length for $P_{90} = 5 \mu\text{s}$ and $P_{180} = 10 \mu\text{s}$. The blue points show what happens if the pulse field amplitude drops by 50% towards the ends of the sensor coil with the sample filling the entire coil.

The plot of intensity against pulse length often fails to reproduce a quality sine wave. Common problems include the following.

- The sample is not fully contained in the sample coil. If the sample is not fully contained in a region of uniform excitation field in the NMR coil, then different parts of the sample experience different pulse lengths. A composite signal is observed. In bad cases, it may be that the signal components conspire to never achieve the zero crossing indicative of a P_{180} . Pulse inhomogeneity can lead to serious artefacts, especially in more advanced experiments such as solid echo and CPMG used to analyse cements. This is relatively serious and normally calls for a smaller sample.
- The power amplifier switching time is long. A non-ideal response will be seen if the rise time and fall time of the power amplifier are relatively long compared to the pulse length, or if the amplifier suffers from droop at sustained high power so that the integrated pulse intensity and hence flip angle is not linear with pulse length.

As a note of caution, remember that the T_2^* value cannot exceed the true T_2 of the sample. If the set-up water sample is over-doped with, e.g. MnCl_2 , then the T_2 will be over reduced making it impossible to shim the magnet. If T_2 is not known, then remember that for a doped water sample $T_2 \approx T_1$ which has just been measured in the context of setting the repetition time. If failure to meet the criterion $T_2^* < T_2$ is suspected, try pure water as a sample.

One further point to note is that some machines offer the option to switch the shims off after an experiment. This helps prevent magnet heating. However, remember that the shims usually take several milliseconds to stabilise after they are switched back on. Ensure that sufficient time is available for this when running actual experiments, otherwise the shim will change during the experiment causing serious artefacts

Finishing off

By now the signal should look like the lower plot in the introductory “What to expect” box. Compared to the start of the set-up, notice that:

- i) It looks approximately like an exponential decay rather than a sine wave - *it is on-resonance*;
- ii) The signal has greater amplitude - *the timing parameters are optimised*;
- iii) All the signal is in the real channel, the imaginary channel is zero - *the receiver phase is set correctly*; and finally
- iv) It extends for a much longer time - *the magnetic field shim is optimised*.

In setting the parameters, it is likely that there will have been some interplay between the different parts of the process. Therefore, without experience, to say that a good set of parameters for the doped water sample has been found, it is advisable to quickly run back through the procedure and make an iterative second pass.

With experience, this second pass, or perhaps otherwise a third pass, can be made using the actual cement sample to be measured, but be warned that some T_2 components (e.g. the hydrate interlayer water) will be less than T_2^* so that further shimming will not be possible. The repetition delay time and receiver gain will need to be re-set due to the different T_1 and ^1H content respectively of cement compared to doped water. Running a known reference sample that mimics cement is a good idea.

A Set-Up Checklist

- Insert a liquid test sample
- Load a single pulse FID experiment
- Set the resonance frequency, f_0
- Set the pulse lengths, t_{p90} and t_{p180}
- Set the repetition delay, τ_{RD}
- Set the number of data points, the sampling interval, and filter
- Set the receiver gain and phase
- Set the number of averages
- Shim the magnet
- Re-set the resonance frequency, f_0
- Does the FID look as expected, as shown in the box “What to expect”?
- Insert a cement sample or reference sample
- Go back, recheck the frequency and update the repetition time, number of data points, sampling rate, filter width, gain, phase and averages for this sample
- Load a “CPMG” or “Solid Echo” experiment as required
- Set the number of echoes
- Set the number of points per echo
- Set the pulse gaps, τ or τ_q
- Record the data.

Using a solid echo to measure crystalline solids in cement

Recording solid echoes

The solid or quadrature echo experiment used to measure very short T_2 solids such as calcium hydroxide or ettringite was described above. Once the spectrometer has been set up as described in the previous section, a cement or reference sample can be positioned in the magnet and settings updated, the solid echo pulse sequence can be loaded and run.

The receiver is turned on, and data need to be collected starting from immediately after the second pulse dead time. In order to capture the solid echo and the first part of the mobile signal, typically 256 data points are recorded with a sampling rate of 1 MHz (dwell time 1 μ s). The receiver filter width needs to be set correspondingly broad, circa 1 MHz. If significantly fewer data are recorded, then it can be hard to separate the mobile signal that is approximately exponential from the tail end of the solid echo decay, especially for larger values of τ_q . If significantly more data are recorded (and included in the analysis) then the non-exponentiality of the T_2^* decay can distort the fitting analysis. The experiment repetition time for signal averaging needs to be ~ 5 times longer than the longest T_1 component in the sample. This component may be either the crystalline solid or free water in large pores. In the absence of water filling large capillary pores, and with a cement with a significant amount of paramagnetic impurities enhancing relaxation, the repetition time can in practice often be as low as $\tau_{rd} = 1$ s or even less. However, ~ 10 s will generally ensure greater quantitative accuracy since the relaxation time of pure bulk water is about 3.6 s. On the other hand, this will greatly slow the data accumulation rate. The optimum τ_{RD} in terms of signal gained per unit time can only be verified by direct measurement of the T_1 relaxation time dispersion.

The experiment needs to be repeated for several values of τ_q . The shortest value of τ_q is limited by the combined 90° pulse length and spectrometer dead-time, the longest by the decay time of the (refocused) solid echo, typically a few tens of microseconds. Ideally, the shortest τ_q should be less than 10 μ s. It is very much a case of the shorter the better. Experience of the authors says that a shortest value greater than 15 μ s yields poor quality data in as much as it is not possible to sensibly estimate the solid intensity because there is too much error in the back-extrapolation to $\tau_q = 0$ required in the analysis. Again, experience says that there is little solid signal left beyond $\tau_q = 55$ μ s and so there is little point using values greater than this. Typically therefore 6 to 10 solid echo experiments are performed with different τ_q values in the range $\tau_q = 10 - 50$ μ s. The values are incremented so as to capture more echoes where the solid signal is greater and it is possible to see its decay best. Ideally, the top of

the echo should be visible at time $2\tau_q$. However, this depends on the combined instrument pulse length and dead time. With good instruments, it is possible to see the echo top for $\tau_q = 12 \mu\text{s}$ or even less. In most cases the top is visible beyond 15 to 20 μs .

Given the signal to noise ratio of a typical bench top low frequency NMR spectrometer, the number of averages (scans) used for solid echo measurements of cement pastes is generally in the range 32 - 128. With a repetition time of 2 s, 64 scans and 6 values of τ_q , the whole process takes 768 s or about 12.5 minutes. For a reference sample as described in this Guide, a larger number of scans is required (i) due to the lower space filling of the reference materials in the probe and (ii) since they are used to calibrate the equipment.

Many spectrometers show a small signal at short decay times for an empty sample tube or empty probe. This signal can arise from small amounts of hydrogen in the probe or tube materials, or even from fluorine that may also be picked up in low frequency / high bandwidth experiments. Therefore an empty tube signal should also be recorded and subtracted from the sample data. Measurement and subtraction of the empty tube signal also helps to remove residual ring down from the probe included in the signal after the nominal dead time.

Analysis of solid echoes

The analysis described below assumes that the real and imaginary components of the solid echo signal from a cement sample or reference material and from an empty sample tube have been recorded as described above.

First, the data should be phased. Many instruments have auto-phasing and this may be used for the cement data. However, where this is done, then it is important that the empty sample tube data are rotated by the same phase angle as the cement data otherwise they cannot be properly subtracted. Where auto-phasing is not available, or proves inadequate, then a few strong data points near the start of the decay are averaged and the phase angle found as:

$$\theta_p = \tan^{-1} \left(\frac{\langle M_I \rangle}{\langle M_R \rangle} \right) \quad (19)$$

where $\langle M_{I,R} \rangle$ is the average of the imaginary/real data points sampled. Thereafter, the phase-corrected real and imaginary data, M'_R and M'_I are found using:

$$\begin{aligned} M'_R &= \cos(\theta_p)M_R + \sin(\theta_p)M_I \quad \text{and} \\ M'_I &= -\sin(\theta_p)M_R + \cos(\theta_p)M_I \end{aligned} \quad (20)$$

If the signal amplitude to noise ratio is sufficiently large and there is no obvious Pake doublet “wobble” to the data, it is often sufficient to calculate the magnitude of the data. The difficulty with low signal to noise is that the baseline becomes equal to the root mean square noise value. The problem with the Pake oscillation is that the phase information inherent in the negative signal is lost.

The phased empty NMR tube signal is subtracted from the sample signal. The subtraction is performed separately for the phased real (M'_R) and imaginary (M'_I) signals.

The individual echo data sets are now fitted to:

$$M'_R(t) = M_{sol} \exp\left(-\frac{(t - 2\tau_q)^2}{T_{2sol}^2}\right) + M_{liq} \exp\left(-t/T_{2liq}^*\right) \quad (21)$$

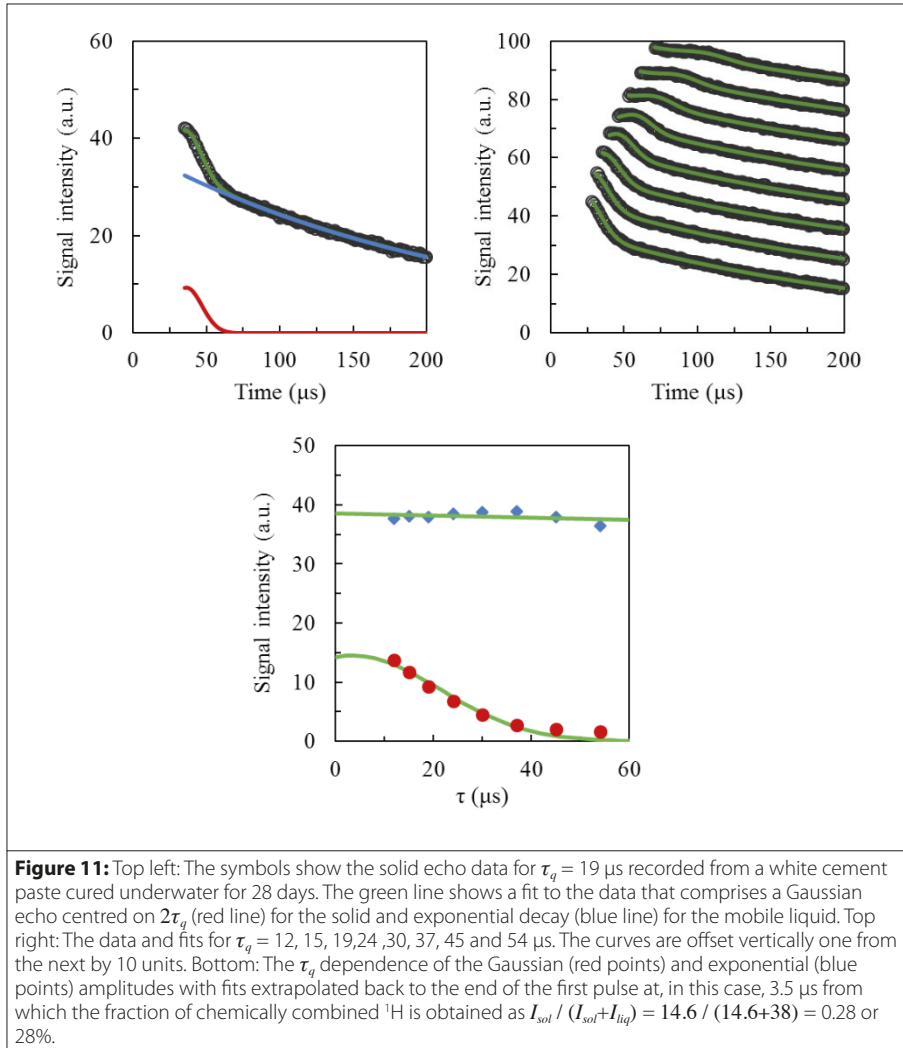
where the fitting parameters M_{sol} and M_{liq} are proportional to the total amounts of solid-bound and evaporable mobile liquid ^1H in the sample and T_{2sol} is a measure

Some tips for successful solid echo analysis

- The full least squares fitting of an echo to a Gaussian and an exponential requires sensible initial estimates of the fitting parameters. If the echo is not well resolved and in particular if the top is not seen, then the fitting can become unstable or the output parameters very dependent on the initial guesses. A useful scheme is to fit first only the back end of the signal, well after the solid component has decayed, to an exponential decay only. The exponential parameters can then be fixed while the front end of the data is fit to a Gaussian and additionally the exponential. If required, a second pass can then be made allowing all four parameters (two amplitudes, two times) to vary. If the echo top is not seen, it may be necessary to fix the Gaussian centre, but take care if the data filtering introduces a time delay.
- The back extrapolation of the solid echo intensities, $M_{sol}(\tau_q)$, to $\tau_q = 0$ is made assuming a Gaussian. However, if only points in the tail of the solid echo decay have been recorded (only long τ_q), due perhaps to a long combined pulse length and dead time, then it can be profitable to measure also a reference sample of known solid ^1H molar fraction I_{sol}^{ref} under the same conditions and to correct the cement solid fraction by a factor $I_{sol}^{ref} / M_{sol}^{ref}$.
- The pulse gap τ_q is usually defined between pulse centres. When the pulse lengths are long compared to the inter-pulse intervals, then better results are obtained by back extrapolation to $\tau_q = t_{p90}$, that is to the point of back-to-back pulses with no gap.
- With good equipment, the wiggle in the time domain data associated with the Pake doublet may be seen. More complex fitting of the Pake doublet as suggested by Bortolotti *et al.* [48] is possible though not usually necessary.

of the non-exponential decay time of the solid. Thereafter the solid echo intensity $M_{sol}(\tau_q)$ are extrapolated back to $\tau_q = 0$ using another Gaussian, equation 11, to find the true solid water fraction I_{sol} (but see the associated text, Figure 11 and the box).

Figure 11 shows some exemplar echoes and associated data fits for a white cement paste mixed at a water to cement ratio by mass $w/c = 0.4$ and cured underwater for 28 days. These data are those recorded by Instrument 1 in the Round Robin Trial reported in Appendix F.



Using CPMG to measure gel and pore water in cement

CPMG data recording

The one-shot CPMG experiment for measuring and separating the evaporable (mobile) water components in cement was introduced in an earlier chapter. Once the spectrometer has been set up as previously described, this experiment can be loaded and run. The first decision to be made is whether to use equally spaced or logarithmically spaced echo times. For cements, logarithmically spaced echoes are suggested, but this option is not always available.

Equal or log spaced CPMG echoes?

- Linearly spaced echoes suffer much less from systematic artefacts due to stimulated echoes arising from unwanted coherence pathways. If the 180° pulses have large systematic errors, such as flip angle error or excitation field inhomogeneity, spurious echo signals can appear using log-spacing.
- Cements have a very broad T_2 distribution. To cover the full range, the first echo time required to study cements is circa $60\text{ }\mu\text{s}$ and the train needs to extend to several tens if not hundreds of ms. Applying many equally spaced refocusing pulses just $60\text{ }\mu\text{s}$ apart for such a long duration can lead to a very high amplifier duty-cycle (perhaps 10 % of time), as well as probe and possibly sample, heating. So-called spin-locking of the mobile, long T_2 components that extends the apparent T_2 is a further potential hazard.
- Unduly increasing the pulse gap for mobile components in larger pores can lead to diffusive attenuation of the echo intensity in the internal susceptibility magnetic field gradients of the sample.
- Notwithstanding the first point, logarithmically increasing the echo spacing for cements analysis has proved to be a good compromise mitigating some of the subsequent disadvantages.

There are various parameters that are commonly used to define logarithmically spaced echo times. They are: the first echo time, $2\tau_1 = 2\tau_{min} = t_{min}$; the last echo time, t_{max} ; the last echo spacing $2\tau_N = 2\tau_{max}$ and the number of echoes, N . They are linked according to:

$$\begin{aligned}\tau_i &= \zeta^{i-1}\tau_1 \quad i = 1 \dots N \\ t_{max} &= 2 \sum_{i=1}^N \tau_i\end{aligned}\tag{22}$$

where ζ is a constant a little greater than 1. The choice of the shortest pulse gap, τ_1 , is based on two factors. First considering the solid signal, it should be greater than circa 30 μ s. Since the crystalline solid signal has an effective relaxation time T_{2sol} of the order of $\approx 10 - 20 \mu$ s, the solid signal is substantially relaxed by the time of the first echo at $2\tau_1$, and does not meaningfully impact the liquid signal. For cements, the zeolitic water in ettringite, in particular, shows a signal with a slightly longer T_2 . However, if $2\tau_1$ is too big, it can affect the analysis of the liquid decay, especially in the very smallest pores – interlayer spaces – of the hydrates that are of the order of 1 nm in size ($T_2 \sim 100 \mu$ s). The interlayer water substantially relaxes before the first echo. For this reason τ_1 should not be greater than $\sim 40 \mu$ s for cement.

The total time span of the echoes needs to be greater than $\approx 5 \times$ the longest T_2 component of the sample. In most cases, a span of a few tens of ms suffices but for fully saturated cements, a few hundreds of ms is required. Typically $N = 256$ or 512.

Another critical factor for CPMG measurements is the signal to noise ratio (SNR) of the accumulated data. The signal to noise ratio increases with the square root of the number of scans. For the purposes of the guide, the SNR ratio is calculated by dividing the intensity of the first echo (S) by the standard deviation of the baseline signal (N). It is recommended that the SNR ratio be greater than 500 in order to achieve an adequate multi-component T_2 fitting analysis by inverse Laplace transformation. Normally this is achieved for cement paste measurements with 512 or 1024 scans or averages. The repetition time between scans is determined exactly as for the solid echo experiment.

Figure 12 shows a typical CPMG echo decay recorded from a white cement paste mixed at $w/c = 0.4$ and cured underwater for 28 days. These data are those recorded by Instrument 1 in the Round Robin Trial reported in Appendix F.

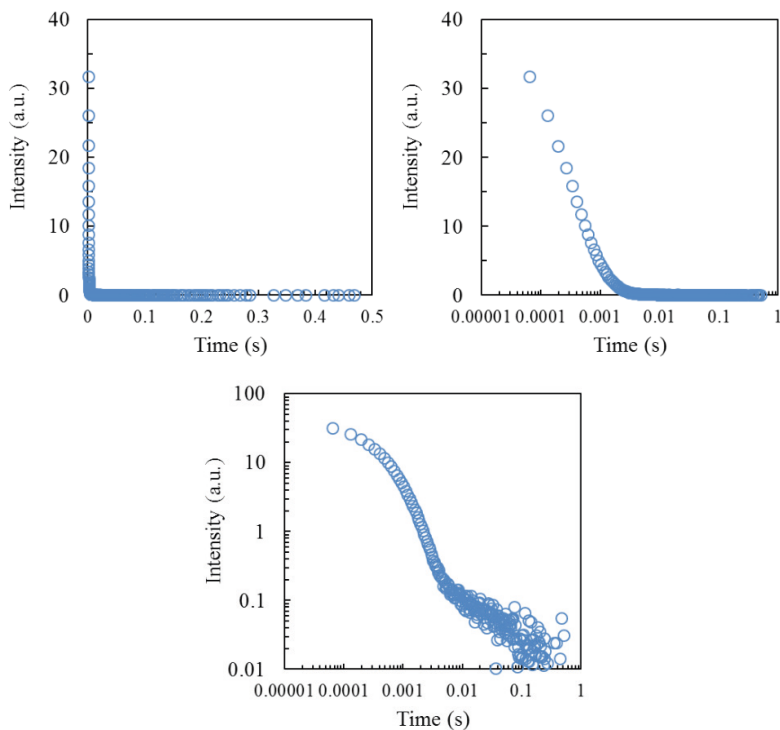


Figure 12: CPMG echo decay recorded from a white cement paste cured underwater for 28 days. The data are shown on linear-linear (top-left), linear-log (top-right) and log-log (bottom) scales. The data are phased and shown in “real-mode” so that negative baseline data points do not show on the log scale. The baseline noise level is circa 0.02.

CPMG data analysis

It is expected that the CPMG echo train intensity decay is described by a quasicontinuous, multi-component distribution of exponential decays each with a different spin-spin relaxation time, T_2 . The objective is generally to identify the relaxation times and the intensity of each component. The integrated intensity should equal that of the mobile component of the solid echo experiment. There are broadly three methods of analysing CPMG echo train data for cements: inverse Laplace transformation; multi-exponential fitting; and exponential stripping. All three have advantages and disadvantages. More detail is given in Appendix B, and Appendix C offers a series of generated data sets that allow the reader to test their own analysis programs. However, the initial data preparation is the same whichever is chosen.

Initial data preparation. The aim is to generate a list of echo intensities against echo times. The echo times are simply given by the series

$$t_j = \sum_{i=1}^j 2 \tau_i, \quad j = 1 \dots N \quad (23)$$

Note, however, that many commercial machines do not by default record these times correctly for log-spaced CPMG – the software provided may assume equally spaced echoes.

The echoes must be phased exactly as the solid echoes were phased. This is especially important if the two data sets are to be quantitatively compared. Any residual baseline signal should be subtracted. However, it is important to ensure that it is baseline signal and not a low-level long T_2 signal component. It is not always necessary to subtract an empty sample tube signal as the empty tube rarely has sufficiently long T_2 components. The exception is if the probe has been contaminated with *e.g.* grease through repeated handling.

Inverse Laplace transformation. In principle, an inverse Laplace transformation (ILT) makes no *a-priori* assumptions about the number, position and widths of the T_2 components or modes in the T_2 distribution of the sample. For discrete data with noise the ILT is an ill-posed problem. Different algorithms to solve it have been proposed by several authors, *e.g.* [49, 50]. All the algorithms require a regularisation parameter that in effect smooths the data to different degrees. Choice and optimisation of this parameter is critical. With too little smoothing, the ILT finds an unreasonably large number of sharp modes; too much smoothing and the actual modes are smeared out. The data analysed in the Round Robin Trial reported in this Guide were processed using the ILT algorithm due to Venkataramanan *et al.* [51]. The authors of this Guide have previously noted that for analysing cements using this algorithm, the integrated area of modes found are accurately reported for reasonable values of the regularisation parameter, though the actual widths varied strongly [4]. Bligh *et al.* [52] have suggested fitting the modes *e.g.* to a series of overlapping log-normal curves. The main disadvantage of using ILT is that very high quality data are required. The SNR ratio must be excellent: typically > 500. Second, it must be free from systematic artefacts.

How is an echo amplitude measured?

The default calculation of an echo amplitude varies from instrument to instrument but is normally also under operator control.

- The amplitude may be taken as the maximum value of the recorded data in the vicinity of the echo centre. This is not advised. If several comparably intense points form the echo centre, then the echo intensity will generally be over-estimated. This introduces a systematic baseline offset error for small signals at large echo time.
- The data point closest to the expected echo centre may be used. The problem with this is that the echo will be delayed slightly due to the actions of filters in the spectrometer. Some instruments take such delays into account automatically, or give the user the option to take them into account manually by introducing small offset data capture delays, but some do neither and action must be taken in data processing.
- The echo intensity may be taken as the sum of a few points around the echo centre. This is a reasonable procedure that can improve the SNR ratio, but note that it introduces a systematic error (when comparing to the solid echo data) if (i) the intensity is not normalised by the number of data points – that is, the data points are not properly averaged, or (ii) the echo amplitude falls away towards the ends of the region of sampled data so the average is systematically less than the central value.
- The few points around each echo centre may be fit to a suitable function such as a quadratic or Gaussian curve in order to determine the central intensity. Indeed, some authors have gone so far as to measure the characteristic echo shape for their instrument and then fit every echo to that shape. By and large, fitting is the preferred method to gain the echo intensities but can be slow unless proven software is available. This is, of course, what is done for the solid echoes discussed in the previous section.
- It is worth checking that for both the solid echo and the CPMG experiments, the echo intensity is normalised to the number of scans (and instrument gain), especially if the number of scans (and instrument gain) is different for the two experiments.

The most common artefacts that can prevent application of ILT are:

- i) A baseline offset;
- ii) Mis-recording of the first echo intensity, perhaps due to contamination by residual “solid” signal;
- iii) A systematic, decaying oscillation in the intensities of the first few echoes due to excitation pulse or magnetic field imperfections, such as in shown in Figure 13 ^[53]; or
- iv) Baseline of insufficient length.

Artefacts are most commonly manifest as spurious peaks outside the range of the recorded echo times, especially at very short times. Put another way, it is not reasonable to expect the ILT to discover relaxation modes substantially outside of the time range of the data. A final problem with the ILT is known as “pearling”. There is a tendency for two close modes in the distribution to be drawn together, raising the relaxation time of the shorter component and lowering that of the longer.

Multi-exponential fitting. Multi-exponential fitting presupposes that one knows how many T_2 modes are to be found in the sample. For cements, it is generally adequate to assume between 3 and 5. The primary three (excluding the solids not seen in the CPMG data) are for the hydrate inter layer water, the gel pore water and the inter hydrate pore water. The next component is capillary pore water that may need to be divided into “large” and “small” if the sample is fully saturated. If multi-exponential fitting of four or five components is attempted with two free parameters (amplitude and relaxation time) for each component, then it is very unlikely that a robust fitting, independent of the initial guess values will be achieved. The fit can be constrained by various means. One that the authors have successfully used is to restrict shortest three relaxation times to be in the ratio 1:3:9 or 1:4:16 based on prior experience of the materials studied. Then the free parameters are reduced to one for the smallest relaxation time and one for each of the amplitudes, giving four for a three-component fit. The fourth (and fifth) component if used is fixed long – several milliseconds – but is usually less critical. Exponential stripping (see below) can be used to estimate the amplitude of these long components prior to constraining them.

Exponential stripping. The idea of exponential stripping is to take the tail of the data only and fit a single exponential decay to represent the longest T_2 component. This fit is then subtracted from the data and a new tail extended back into the data. The procedure is repeated iteratively until the data have been completely fitted. The primary difficulty with this method is that the results can depend significantly upon where the tail cuts are made. Notwithstanding, the method was used by Plassais *et al.* ^[54] in a widely cited study.

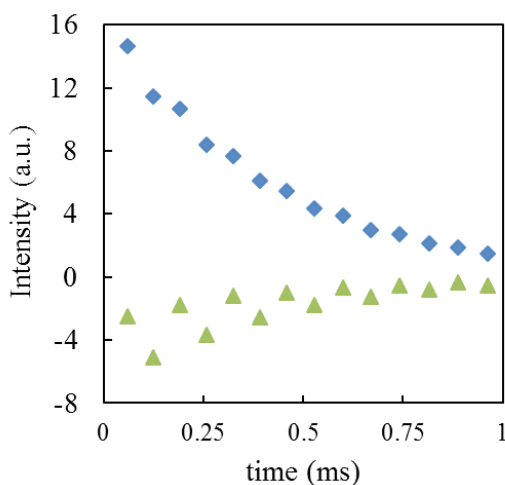


Figure 13: Spurious oscillations seen in the first few echo intensities of a CPMG train. The oscillations are most commonly an artefact due to pulse flip angle error caused by excitation pulse field inhomogeneities. The oscillations are seen most strongly in the (ideally zero) imaginary component of the signal (green triangles), but are most troublesome in the real data (blue diamonds) where, due to the rapid signal decay, they are not always noticed. The oscillations lead to systematic errors in the inverse Laplace analysis of the mobile water fractions.

ILT or Multi-exponential fitting?

- ILT is best suited to high quality data when the underlying T_2 distribution is unknown. It has primary application to the study of unknown materials and makes no *a priori* assumptions about the results. However, it is highly susceptible to artefact and must be used with caution.
- Multi-exponential fitting, including constrained and stripping versions, is suited to lower quality data when there is some knowledge of the underlying T_2 distribution. It has primary application to the study of known or partially known materials. It works well for elucidating trends across multiple data sets such as time course series.

Figure 14 shows the results of an ILT analysis of the data presented in Figure 12. The middle line is for the optimum value of the regularisation parameter α found according to the method given in ^[51]. The other lines are for changing this parameter by a factor of 100, both larger and smaller. The peak widths vary significantly with the regularisation parameter but their integrated areas do not, especially if α is too large – see Table 1. If the smoothing is too great, peaks merge as shown in Figure 14. Figure 15 shows a constrained multi-exponential fitting analysis of the same data. In this case, the constraints are that the $3T_2$ times are in the ratio 1:3:9. The peak intensity fractions and T_2 values are given in Table 1.

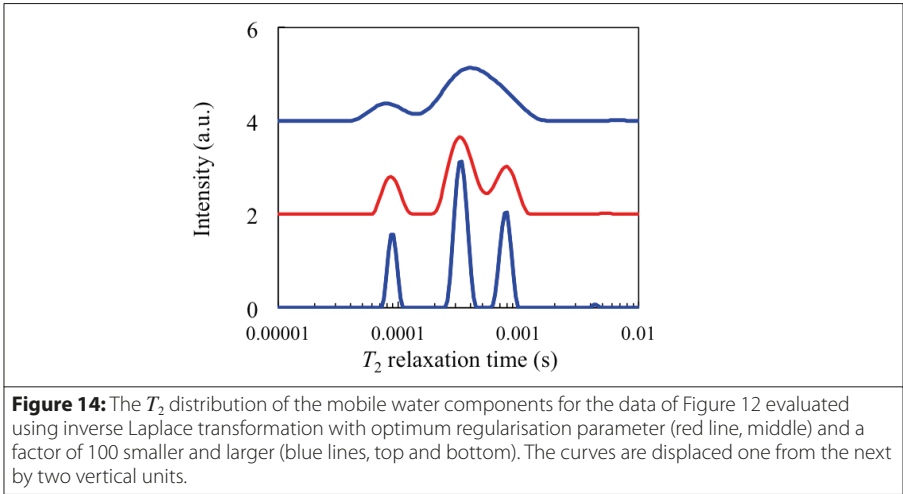


Figure 14: The T_2 distribution of the mobile water components for the data of Figure 12 evaluated using inverse Laplace transformation with optimum regularisation parameter (red line, middle) and a factor of 100 smaller and larger (blue lines, top and bottom). The curves are displaced one from the next by two vertical units.

Table 1				
	Crystalline solids	Hydrate interlayer	Gel pores	Interhydrate pores
ILT $100\alpha_{opt}$	28 %	13% at 90 μ s	37% at 340 μ s	22% at 800 μ s
ILT α_{opt}	28 %	13% at 90 μ s	38% at 320 μ s	21% at 800 μ s
ILT $0.01\alpha_{opt}$	28 %	11% at 80 μ s	60% at 410 μ s	-
Multi-exp. fit	28 %	25% at 167 μ s	42% at 500 μ s	6% at 1505 μ s

Table 1: The weighting of the different water reservoirs in a cement sample determined from different analyses (see text). Water bound in crystalline solids from the solid echo experiment is shown in column 1. The remaining columns are based on inverse Laplace transform or exponential fitting of the CPMG data weighted to the total mobile fraction from the solid echo experiment.

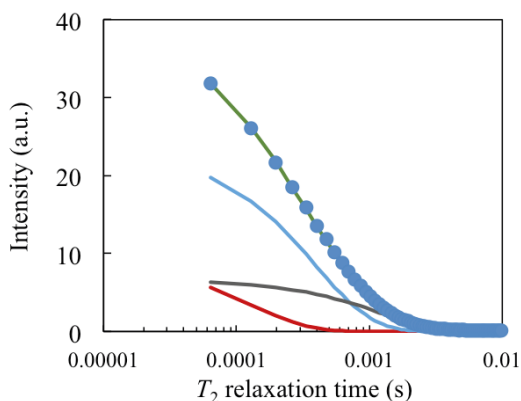


Figure 15: The CPMG fit for the same white cement data as Figure 12 based on constrained multi-exponential fitting. The fit is shown decomposed into its three components (red, blue, and grey).

Combining the solid echo and CPMG data

The final step of the analysis is to divide the mobile fraction measured in the solid echo experiment into its own sub-component fractions identified in the CPMG experiment. As a check the total CPMG amplitude should equal that of the mobile component in the solid echo experiment.

The obtained signal fractions can be used to determine the hydrated cement composition and density of cement hydrates, as shown in Appendix D.

An analysis check list

Solid echoes:

- Subtract the empty cavity signal.
- Phase the data.
- Fit the individual echoes to a Gaussian centred on $2\tau_q$ and an exponential.
- Extrapolate the echo and exponential amplitudes back to zero pulse gap.
- Calculate the crystalline solid and mobile water fractions.

CPMG:

- Subtract the empty cavity signal.
- Phase the data.
- Calculate the echo amplitudes as a function of time.
- Check for systematic errors such as oscillations in the first few amplitudes and / or baseline offset.
- Fit echo amplitudes to a multi-modal exponential decay or use an inverse Laplace transformation.
- Identify each component in the fit with water in a different pore size.
- Divide the mobile fraction of the solid echo according to the CPMG distribution and check the total adds up to 100%.

Reference materials

- Introduction
- Sintered alumina and calcium hydroxide
- Exemplar results

Introduction

Reference materials are required in order to test that both the NMR and data analysis procedures are working correctly and calibrated as expected. Reference samples are often provided with NMR spectrometers in order, *e.g.* to set the resonant frequency and pulse length and/or amplitude and shim the magnet as described in the previous section. However, these samples are often far from ideal for ensuring that experiments and analysis procedures to study cement are optimised. Many are single component liquids with a single long T_2 component. The extremely broad and multicomponent relaxation distribution of cement and the fact that the T_2 relaxation rate of the dominant components is comparable to the field inhomogeneity of many bench top magnets makes the choice of comparable reference materials especially important. A carefully prepared cement sample could be used as a reference material. However, it is a poor choice for two primary reasons. First, since hydration continues, and therefore the T_2 distribution evolves, for a very long time, the sample is not long-term stable. Second, because the raw natural materials from which cement is made vary greatly, the cement is not reproducible from laboratory to laboratory. The experience of the authors is that there are few materials available which both mimic the NMR response of cement and fulfil the criteria of being stable and reproducible. Appendix E details a study to identify and to make such materials, while the calculation to determine mass fractions of reference material components are presented in Appendix D. The remainder of this section summarises the output of that study.

Sintered alumina and calcium hydroxide

Resultant from the study described in Appendix E, it is found that weakly sintered α -alumina pellets, saturated with a slightly acidic aqueous solutions of MnCl_2 , are suitable for use as reference materials that mimic the pore water of cements. Samples are made from sub-micrometre α -alumina powder formed into cylindrical shapes using pellet press dies at a pressure of a few bars and sintered at 1000 °C. Water confined in the pores of sintered alumina relaxes more quickly than bulk water as expected. However, the relaxivity is not as fast as in cement partly because the pores are of different size and partly because there are fewer paramagnetic ions. The relaxation time can be fine-tuned by the addition of paramagnetic ions. Hence, the samples are saturated with MnCl_2 doped water stabilised by the addition of a small amount of nitric acid. Three cylinders with different solution concentrations and overall mass are required to mimic the three primary T_2 mobile water components of cement: hydrate interlayer water, hydrate gel pore water and interhydrate capillary pore water. Differing mass is required to change the relative amount of the three components.

It is further found that calcium hydroxide can be used as a reference material for the crystalline solids. Since it has a tendency to adsorb water, it is necessary to pre-dry the material and keep it in a sealed container.

Thus, a suitable reference comprises a composite of four samples isolated one from the next in sealed glass tubes as shown in Figure 16. Further details of the sample manufacture are given in Appendix E.

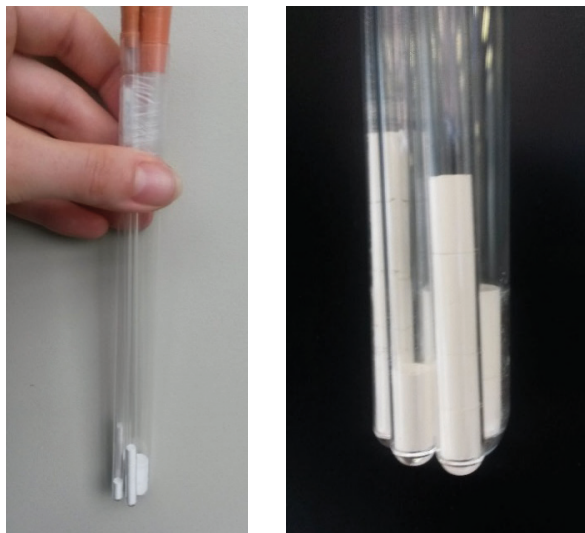


Figure 16: A four component reference sample.

It is noted that a reference sample of this sort is, of course, four separate samples. The advantage of this is that each component is isolated from the next and stable in its own right. Each can be fine-tuned to a specific relaxation time and overall signal fraction. The primary disadvantages are that different spatial parts of the sample necessarily experience slightly different excitation pulse flip angles and receiver sensitivity due to spatial inhomogeneity of the radio frequency sensor coil and a different magnetic field strength due to inhomogeneity of the magnet. These variations can lead to intensity (*i.e.* signal fraction) and relaxation time estimation errors. A further disadvantage is that the glassware required to keep the samples separate takes a substantial fraction of the total available space. Therefore, the overall signal per unit volume is significantly lower for a composite reference compared with a comparable volume of cement. The authors are not aware of a spatially homogeneous or even quasi-spatially homogeneous material that mimics cement from the standpoint of NMR and that is both readily reproducible and stable.

Exemplar results

Figures 17 and 18 show the results of a series of solid echo and CPMG with logarithmic pulse spacing experiments that were performed on a four-component composite doped α -alumina, calcium hydroxide reference sample. The four samples were contained in three 3 mm and one 5 mm diameter tubes, filled to a maximum depth of 30 mm and placed side by side in a square formation. The tubes are filled to different depths so that the liquid volumes mimic the water fractions in different cement environments. The concentrations of acidic MnCl_2 solution used to achieve the cement characteristic T_2 relaxation times are 12, 75 and 250 mM. The measurements were made using a 20 MHz bench top spectrometer with a standard 18 mm probe (Instrument 1 of the Round Robin Trial). The sample was fully contained within the active volume of the probe. The sample was measured and analysed exactly as described in the previous chapter using both inverse Laplace transformation and constrained exponential fitting for the CPMG.

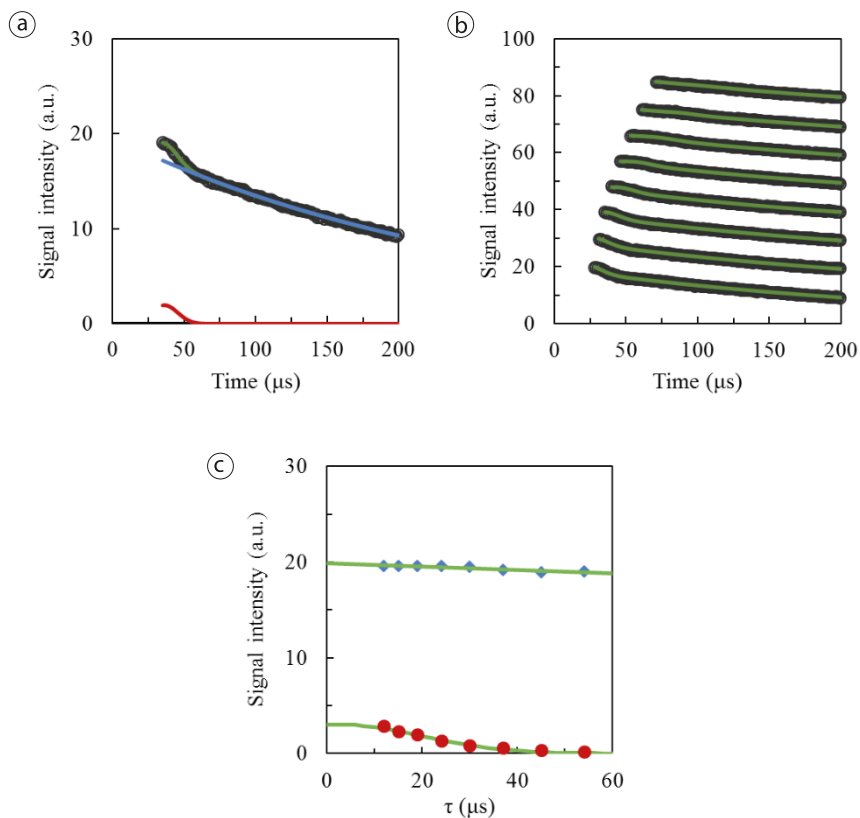


Figure 17: a: The symbols show the solid echo data for $\tau_q = 19 \mu\text{s}$ recorded from a reference sample as described in the text. The green line shows a fit to the data that comprises a Gaussian echo centred on $2\tau_q$ (red line) for the solid and an exponential decay (blue line) for the mobile liquid. b: from bottom to top, the data and fits for $\tau_q = 12, 15, 19, 24, 30, 37, 45$ and $54 \mu\text{s}$, offset vertically one from the next by 10 units. c: The τ_q dependence of the Gaussian (red points) and exponential (blue points) amplitudes, with fits extrapolated back to zero actual pulse gap ($\tau_q = 3.5 \mu\text{s}$).

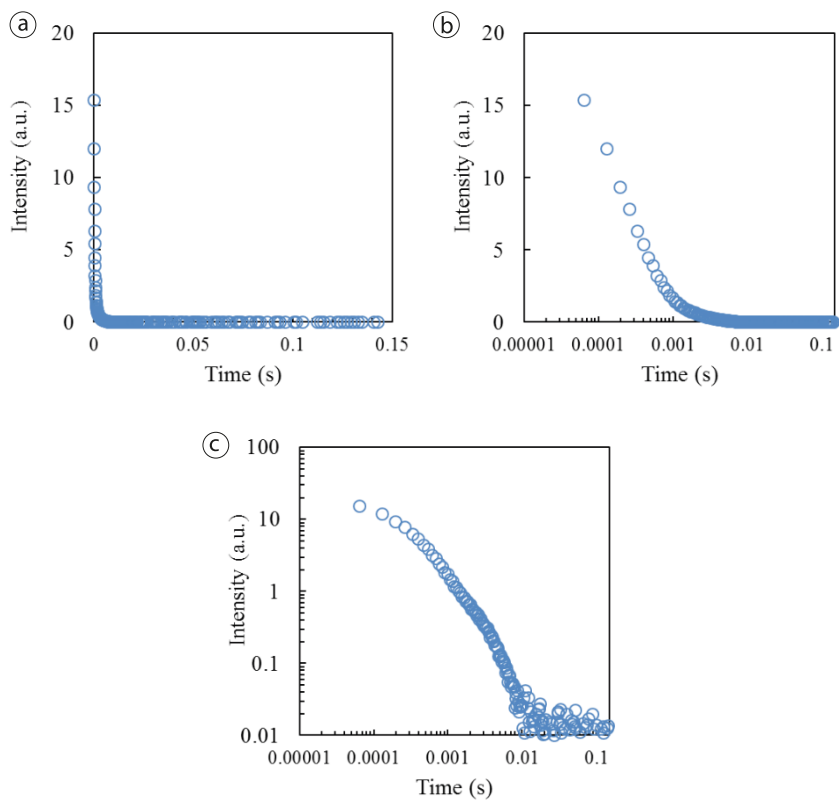


Figure 18: CPMG echo decay recorded from a reference sample. The data is shown on linear-linear (A), linear-log (B) and log-log (C) scales. The data are phase corrected and shown in “real” mode so negative baseline data points do not show on the log scale. The baseline noise level is circa 0.02.

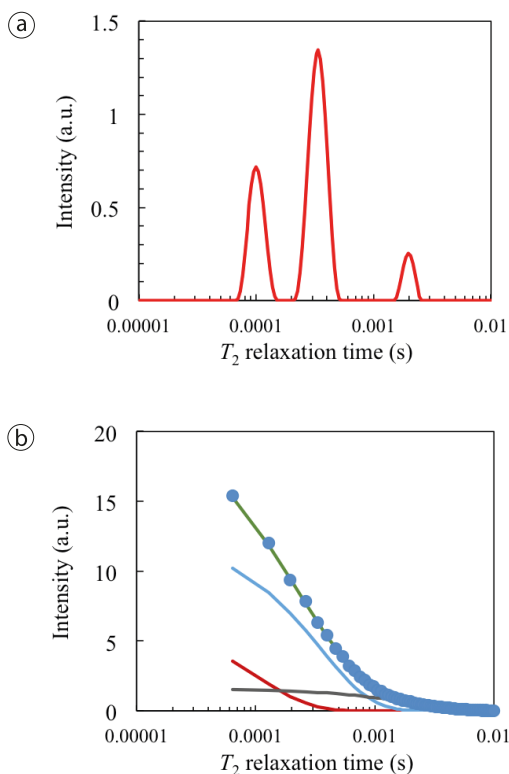


Figure 19: a: the T_2 distribution for the mobile water fractions in a four-component (one solid, three mobile) reference sample. The CPMG data were analysed using inverse Laplace transformation. b: an unconstrained multi-exponential fit to the same data.

Figure 19 shows the fit results. Table 2 shows the intensities measured by the different methods and compared to the known gravimetry. The solid intensity from the solid echo experiment is also included in the table. There is a high degree of agreement between the inverse Laplace transformation, the *unconstrained* multi-exponential fitting and gravimetry.

For instrument 12 of the Round Robin Trial, a different (smaller, 10 mm probe) four component reference sample was prepared and measured both as a composite and also as four individual samples. The T_2 and intensity values obtained from this set of samples are compared in Table 3.

Table 2

	Solids	Mobile 1	Mobile 2	Mobile 3
Gravimetry (molar fraction ¹ H)	12.6%	24.7%	55.3%	7.5%
ILT	13.5%	25.7% at 100 μ s	54.2% at 340 μ s	6.5% at 1970 μ s
Multi-exp. fit	13.5 %	28% at 110 μ s	52% at 350 μ s	7% at 2000 μ s

Table 2: Collected results and comparison to gravimetry for a reference sample composed of four components: calcium hydroxide and three differently doped sintered α -alumina pellets.

Table 3

	Solids	Mobile 1	Mobile 2	Mobile 3
Gravimetry	18.2%	26.5%	29.6%	24.8%
ILT individual samples	18.5%	27.3% @ 115 μ s	29.3% @ 350 μ s	24.9% @ 2150 μ s
ILT	16.6%	26.7% @ 115 μ s	31.4% @ 350 μ s	24.8% @ 2360 μ s
Unconstrained multi-exp. fit	16.6%	28.3% @ 121 μ s	28.7% @ 380 μ s	24.0% @ 2470 μ s
Constrained multi-exp. fit	16.6%	26.9% @ 115 μ s	29.1% @ 350 μ s	25.0% @ 2360 μ s

Table 3: Results for a reference sample comprising calcium hydroxide and three differently doped sintered α -alumina reference samples compared to the components measured individually.

A Round Robin analysis

- Objectives
- NMR experiments
- Materials
- Results

Objectives

A Round Robin Trial² of the methods advocated in this report was organised. The purpose of the Round Robin Trial was to test the practicality, reproducibility and accuracy of T_2 CPMG and solid echo NMR measurements and analyses of cements based on the good practice described in this guide. The Round Robin Trial involved eight European laboratories spread across academia, industrial research and development laboratories belonging to cement and cement additive manufacturers, and NMR equipment manufacturers. Some laboratories offered more than one instrument so that a total of twelve instruments was used. The laboratories and instruments were chosen in order to represent a range of systems of different specification (sample size, field strength, pulse length, etc.) and age, from a range of commercial manufacturers as well as home-made equipment.

NMR experiments

The available equipment covered the frequency range from 2.5 to 23.5 MHz. Probe sizes ranged from 10 mm up to 50 mm diameter. The characteristics of the equipment used are summarised in Table 4. The table includes the operating frequency, probe dimensions, radio frequency pulse lengths and dead time of the different instruments. It was not possible to perform all the experiments exactly as described in the proposed good practice at each site. Also, it was not possible to perform all experiments on all materials at each site. In particular, instrument 9 was not used to measure cements since the probe was too large. Tables 4 and 5 detail the precise experiments performed, the associated parameters and the materials used. The objective in this Guide is to use the results to highlight critical aspects of the procedure.

Materials

Reference materials

Four component reference samples comprising calcium hydroxide and three samples of sintered α -alumina doped with MnCl_2 solutions of different strength as described in the previous chapter were prepared. Each component was contained in a separate sealed tube, then all four tubes placed side by side in a square array in the spectrometer. The filling factor, that is the ratio of actual sample to probe volume, was therefore small, typically 20 – 50%.

² The Round Robin Trial was jointly funded by a UK Engineering and Physical Sciences Research Council Impact Acceleration Account held at the University of Surrey and by the National Physical Laboratory.

Cement pastes

Cement pastes were prepared using white Portland cement (Cem I 52.5 N), grey Portland cement (Cem I 42.5 N) and slag cement (Cem III/B 32.5 N-LH/SR). The mineralogical composition of the cements was determined by X-ray diffraction³. The compositions are presented in Table 5.

Cement powder (80 grams) was mixed with distilled water at two water-to-cement (w/c), ratios by mass: 0.4 and 0.46. The mixing was performed in three steps: i) 3 minutes mixing at 500 rpm; ii) 2 minutes resting during which the paste was covered; iii) 2 minutes mixing at 2000 rpm. This is the procedure recommended by Nanocem for the analysis of cement pastes during two European Union Marie Curie Training Network Programmes. Freshly mixed paste was placed directly in glass NMR tubes using a plastic pipette. The size of samples varied by instrument dependent upon the probe size as listed in Table 4. Five hours after mixing, samples were covered with a small quantity (~2 – 3 mm) of saturated calcium hydroxide solution and the tubes sealed with Parafilm®. Samples were cured at 20 °C for 30 ± 2 days before measurement for all instruments except numbers 1 and 2 that were cured for 50 days. The solution above the samples was removed before NMR measurement.

NMR methods

Solid echo and CPMG experiments were performed on the different samples using the procedures described in Chapter 2. For solid echo experiments, 32 scans (averages) were collected for each τ_q for cements and 512 scans for reference samples. The solid echo experiments were not performed using instruments 1, 8 (and 9). Unless specified otherwise in Table 4, the CPMG experiments were carried out with logarithmic echo spacing. Various, 512 and/or 1024 scans were collected for cement pastes and 8192 scans for reference samples. The CPMG echo train decays were analysed using both inverse Laplace transformation and constrained multi-component exponential fitting. Other parameters for the different instruments and experiments are presented in Table 4. These parameters were generally chosen to be as close as possible to those recommended in this Guide, within the constraints of the available instrumentation. Instrument 9, which had a 50 mm probe, was not used to measure cement pastes.

³ The XRD experiments were performed at the Laboratoire des Matériaux de Construction, EPFL in collaboration with Dr A. Muller. A Panalytical X'Pert Pro MPD diffractometer with a CuK α source (wavelength 1.54 Å) and a fixed divergence slit of 0.5° was used. Samples were scanned using an X'Celerator detector between $2\theta = 7^\circ$ and 70° . The rotation step size was 0.0167° (2θ) and the time step was 77.5 s.

⁴ www.nanocem.org; EC FP6 RTN NANOCEM Project Number 19283 and EC FP7 ITN TRANSCEND Project Number 264448.

Table 4: NMR instruments and experimental parameters used for the Round Robin Trial.

Instrument	1	2	3	4	5	6	7	8	9	10	11	12
¹ H frequency (MHz)	20.0	3.0	20.0	20.0	8.0	7.5	23.5	2.5	10.7	23.4	23.4	20.0
Probe sample temp. (°C)	22	22	30	24	30	20	24	15	28	40	40	30
Probe diam. (mm)	18	38	10	10	24	10	18	20	50	10	26	10
Sample length (mm)	30	50	10	8	30	10	30	30	50	7	25	10
P_{90} length (μs)	3.5	8.1	2.3	3.9	8.5	2.9	6.4	10	12	2.6	6.9	5.5
P_{180} length (μs)	7	16.2	4.5	7.8	17	5.5	12.8	10 ^a	12 ^a	5.2	13.8	5.5 ^a
Deadtime (μs)	15	15	9	20	20	15	10	65	80	8	11	15
Experiments												
Dwell time (μs)	1	1	1	1	1	1	1	1	1	1	1	1
Repetition delay (s)	1	1	1	1	1	1	1	1	1	1	1	1
Solid echo	-	✓	✓	✓	✓	✓	✓	-	-	✓	✓	✓
τ_q (μs)	-	12-54	12-54	24-55	30-55	12-37	12-54	-	-	12-54	12-54	12-54
Linear spaced CPMG	-	-	-	-	-	-	-	-	-	✓	✓	-
Log spaced CPMG	✓	✓	✓	✓	✓	✓	✓	✓	✓	-	-	✓
$2\tau_1$ (μs)	32	64	32	32	32	26	32	88	88	32 and 256 ^b	64	32
τ_n (μs) ^c	5000	5000	5000	5000	5000	5000	3000	5000	5000	-	-	5000
No. of echoes, N	256	256	256	256	256	256	256	256	256	1024	1024	256
No. data points/echo	8	8	1	1	1	1	4 or 8	32	4	4	4	32

a The 180° pulse amplitude is circa 6 dB greater than the 90° amplitude;

b Two data sets were recorded with different linear spacing for a greater overall range and interleaved in the analysis;

c For reference materials, $\tau_n = 1000 \mu s$ in all cases.

Table 5: The composition of anhydrous cements used to prepare materials for the Round Robin Trial										
Phase/cement type	Alite C ₃ S	Belite C ₂ S	Aluminate C ₃ A	Ferrite C ₄ AF	Portlandite CH	Gypsum CH ₂	Bassanite CH0.5	Calcite CC	Amorphous	Total
White Portland	62.9	19.1	7.2	-	2.4	-	5.2	2.2	1	100
Grey Portland	68.2	3.2	5.6	8.1	-	3.9	4.5	-	6.4	100
Slag cement	19.5	1.6	0.7	1.6	-	6.5	2.9	-	67.1	99.9

Results

A key limitation of the Round Robin is that different samples needed to be prepared for each instrument due to the variety of probe sizes used and the fact that different instruments were available at different times over an extended period. Therefore, results on the “same” samples from different laboratories cannot be compared. Rather each has to be interpreted given the known composition, and in the case of cements, age, of that sample.

Reference materials

The chemically combined water fraction. Figure 20 shows the mass fraction of chemically combined water measured by NMR solid echo against the mass fraction calculated from the gravimetrically measured composition of the samples. The chemically combined water is that which is incorporated in the calcium hydroxide. Each data point on the graph is from a different composite sample measured with a different test instrument. The chemically combined water fraction by NMR accurately reflects the chemically combined fraction by mass across the majority of samples and instruments since the data points lie on a diagonal line. In Figure 20, the data point for mass fraction $\approx 58\%$ is a noticeable outlier. It is believed that there is an error in the gravimetry of this sample as this instrument (Instrument 3, red circle in Figure 20) has a short dead time and otherwise behaves as expected. Two other experiments that lie off the diagonal line reflect the criticality of certain experimental parameters, in particular the need for a short first echo time (instruments 4 and 5, red triangles in the Figure).

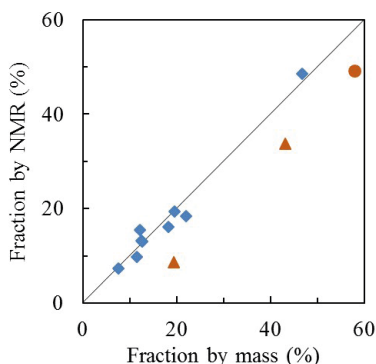
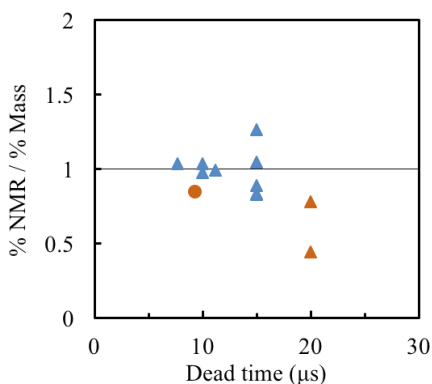


Figure 20: The solid fraction (^1H in $\text{Ca}(\text{OH})_2$) determined by NMR against the calculated fraction based on gravimetry for reference materials measured at different laboratories. All but three of the data points (blue diamonds) lie on the diagonal line with a coefficient of determination of $R^2 = 0.970$. The remaining three points lie significantly below the line (red triangles and circle). These three are discussed further in the text.

The importance of a short solid echo time.

The solid echo data points for reference samples with chemically combined water mass fractions $\approx 20\%$ and 43% (see Figure 20) were made using instruments 4 and 5. For these instruments, the shortest τ_q was equal to 24 and 30 μs respectively due to a long receiver dead time. This is significantly longer than for other instruments. At these long values of τ_q , the solid signal is already significantly attenuated, leading to large experimental uncertainties when the data are back extrapolated to $\tau_q = 0$. To reinforce this observation, the figure below shows the ratio of the NMR to gravimetric measured chemically combined water content for each instrument as a function of the instrument dead time. It is clear that as the dead time increases, so does the uncertainty in the result. Good results are only obtained for a dead time of 12 μs or less.



The ratio of chemically combined water fraction measured by NMR intensity and calculated from gravimetric data for reference samples as a function of spectrometer dead time. The data should lie on the horizontal line where the ratio = 1. It is seen that the larger the dead time, the larger the uncertainty. The data markers correspond to those in Figure 20.

Differentiation of different mobile water fractions. Figure 21 presents the division of the mobile water signal across reference material mobile components determined by CPMG NMR against that determined from gravimetric data for different instruments. The analysis is made using inverse Laplace transformation. The samples are the same as those presented above and so each has four components including the solid. However, the solid component is excluded from the analysis here so that the sum of the three mobile components is 100%. In every case, the data are expected to lie on the diagonal line.

As expected, the three mobile water components are identified by all instruments used. The first and second components, Figures 21a and b respectively, are reasonably accurately determined by NMR by all but three instruments. These components have the shorter T_2 values and are designed to mimic the inter-layer and gel-pore water of cements. A good agreement is found for the third component (Figure 21c) that mimics the capillary water of cement across all but one of the instruments. The exception is instrument 3, discussed below. Since in reality most interest focuses on an ability to distinguish water in cement hydrates from that in capillary pores, it follows, and we note, that there is also good agreement *between the sum of the first and second component fractions* measured by NMR and the sum measured by mass (Figure 21d). Hence, where anomalies occur, it is mainly in an ability to separate accurately the first two components.

We now consider the instruments and samples for which there is disagreement between the NMR and gravimetrically determined mobile fractions for the first and second components. The three instruments that poorly reflect these amounts are the same as those that poorly reflected the solid fraction. They all used $32\ \mu\text{s}$ for the first CPMG τ_1 , which is deemed good. The dead time for instrument 3 is low ($9.2\ \mu\text{s}$) although for instruments 4 and 5 it is significantly longer at $20\ \mu\text{s}$. Only one data point per echo was recorded. However, this is not overly unusual (e.g. it is the same as instrument 6) and the data sets all have an acceptably high signal to noise ratio, which is also good. As it stands the authors are unclear why these points are such outliers. In the case of instrument 3, it may be due to sample gravimetry, as previously discussed. The data measured with instruments 4 and 5 has been re-analysed by using an alternative inverse Laplace transformation algorithm, UPEN,^[55]. The fractions of components obtained using UPEN for instruments 4 and 5 are in better agreement with gravimetry with less than 6% absolute difference compared to using the algorithm due to Venkataramanan *et al.*, as elsewhere in this report. The detailed origin of the discrepancy is unclear, but probably lies in the differences in details of the data smoothing.

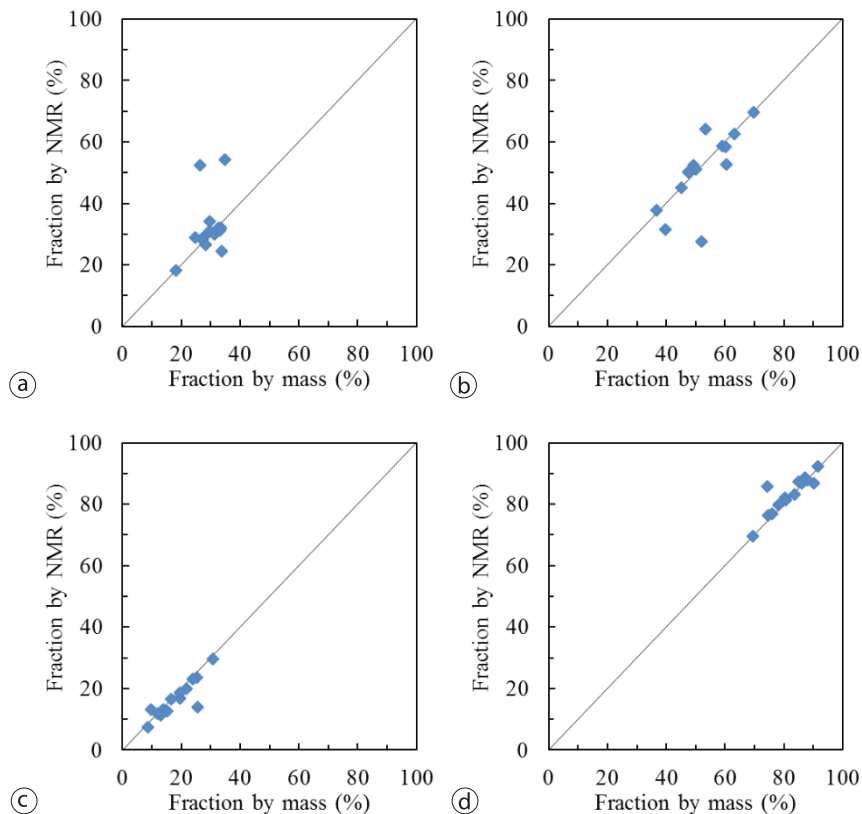


Figure 21: The fractional split of the: (a) first; (b) second; and (c) third mobile H₂O relaxation components for reference materials as measured by NMR (ILT analysis) against the same fractions determined from gravimetric data using different instruments. (d) Shows the sum of the first and second components. The solid is excluded from the division so that the sum of the three components is 100% in all cases.

Reproducibility of the measured T_2 relaxation times. The T_2 relaxation times of the different mobile components for the reference materials are consistent across the laboratories and instruments as shown in Figure 22. The dependence of T_2 relaxation time on frequency is presented in Figure 23. No significant frequency dependence is seen in the range examined.

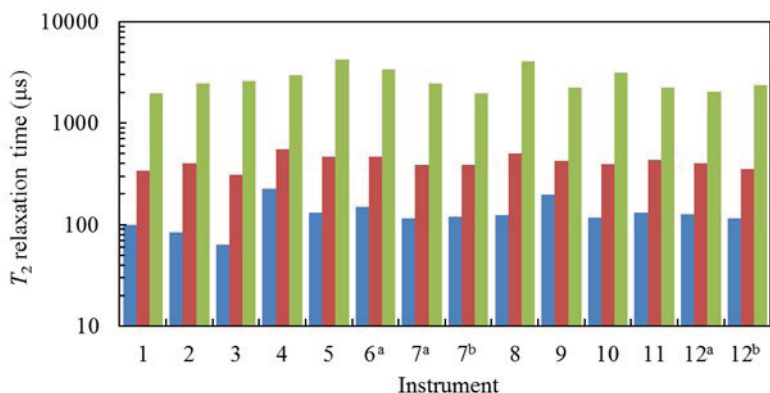


Figure 22: The central values of the multi modal T_2 relaxation time distribution for mobile ^1H components determined by inverse Laplace Transformation analysis for reference samples measured using different instruments. ^a, gives the results of an experiment using four contacting sample pellets freshly put into a tube. ^b, is for the otherwise standard procedure of four samples in separate tubes.

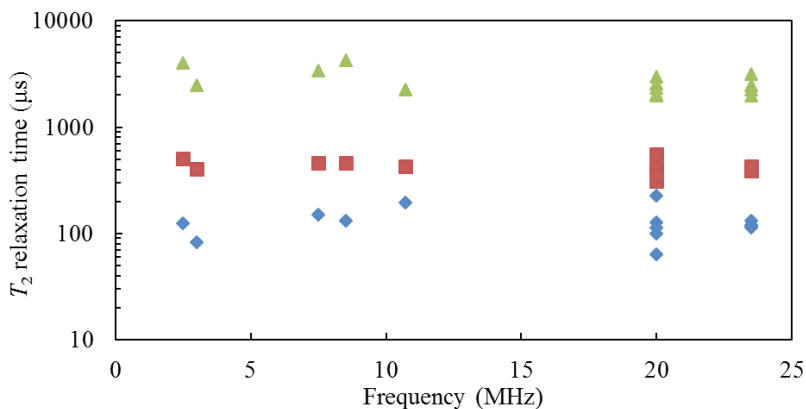


Figure 23: The central values of the multi modal T_2 relaxation time distribution for mobile ^1H components determined by inverse Laplace transformation analysis for reference samples as a function of measurement frequency.

General observations concerning CPMG and reference materials.

A note on excessive averaging, long experiments and temperature instability:

Data for instruments 8 and 9 were recorded with 512 scans (instrument 8: 20 mm probe) or 1024 scans (instrument 9: 50 mm probe). A second data set was then recorded with 8192 scans (both instruments). One expects that more scans offer a better result. However, for both probes, the distribution of shorter components does not improve when the number of scans is increased. The most probable reason amongst many is that these magnets were not temperature stabilised and that the magnetic field drifted appreciably during the longer experiments. Only the results for the smaller number of scans are presented here.

A note about contacting samples:

The data measured using instrument 6 for the reference material prepared as everywhere else as an assembly of four sealed tubes, are not presented due to a very low signal to noise ratio (< 100). Rather, to increase signal, results are presented for an assembly of contacting pellets of material placed in one tube and measured immediately thereafter. Data collected elsewhere leads to the conclusion that, with time (hours to days), such a sample would not be stable. Contacting samples were additionally measured in instruments 7 and 12, and these data are also included in Figure 22.

A note about unconstrained multi-component exponential fitting analysis:

The complete analysis of the same CPMG data sets was also performed using unconstrained three-component multi-exponential fitting in Origin®. Despite very good coefficient of determinations (R^2) for individual fittings, the resultant data showed considerably more scatter for NMR mass fraction versus gravimetric fraction of different components compared to the results from inverse Laplace transform analysis. Notwithstanding, with unconstrained multi-exponential fitting, the determination of the third component is considerably better than either of the first two. In consequence, the sum of the first two is equally good. This indicates that the primary difficulty is, as with inverse Laplace transformation, in separating the intensity of the two short components, one from the other.

The T_2 relaxation times determined by multi-exponential fitting are in general slightly higher than those found from inverse Laplace transformation. On average the difference is 5%, but it is as high as 15-20% for all components using instrument 7 (with the sample made from contacting pellets) and for the first component using the instrument 8. Nevertheless, the same frequency independence of T_2 is found with multi-exponential fitting as with inverse Laplace transformation.

Cement pastes

Here we consider the results for just the grey Portland cement samples mixed at water to cement ratio $w/c = 0.40$ and cured underwater for nominally 28 days (50 days for instruments 1 and 2), and make some overview comments with regard to the rest. Detailed results for all the pastes are presented in Appendix F.

Water in nano-crystalline phases. Figure 24 shows the molar fraction of water in nano-crystalline phases such as calcium hydroxide and ettringite of grey Portland cement pastes. The fractions are determined from NMR solid echo measurements (blue bars) across all the instruments available that could do this measurement. The mean and standard deviation are $22.8 \pm 5.4\%$ for $w/c = 0.40$. The large standard deviation evidences that there is variation in the measured fraction across the instruments, though much of the variation is attributed to instrument 5 with results that are substantially out of line with the remainder. Excluding instrument 5, the mean and standard deviation are $24.5 \pm 2.5\%$. The wide distribution is partly attributable to differences in instrumentation, as explained for the reference materials, and partly to differences in the samples. Since curing is underwater, additional water is drawn into the sample to fill the voids created by chemical shrinkage. Hence the content of water within the paste changes during curing. However, due to the diminishing permeability of the samples as they cure, the extent to which the mobile water and hence total water increases so lowering the fraction of chemically combined water in crystalline solid phases, and the extent to which additional hydrates grow, is dependent on sample size (diameter and length) ^[46]. The post-curing total water content of samples ($g_{\text{H}_2\text{O}}$ per $g_{\text{anhyd.-cement}}$) was calculated gravimetrically post-curing. This varied from 0.419 to 0.445. However, the gravimetric mass calculation ignores the fact that individual samples are inhomogeneous on a microscopic scale.

Mobile water in pores. Figure 25a shows the distribution of T_2 relaxation times of mobile ^1H in the grey Portland cement pastes mixed at $w/c = 0.40$ determined from inverse Laplace transformation of NMR CPMG T_2 decays. The decays were recorded using log-spaced experiments except for instruments 10 and 11 for which linear spacing only was available. The distributions typically comprise a series of peaks in the range 0.08 to 3 ms and some other features, as discussed below. In general, three components are identified and their relative intensities are shown in Figure 25b. The first component has a typical T_2 of about 100 μs , the second of 300 - 500 μs , and the third of 1 - 2 ms, as shown in Figure 25c. A small fourth component is included in Figure 25b that sums over all peaks with T_2 higher than 5 ms. Chemically combined water, as discussed in the preceding paragraphs, is excluded, so that the components add to 100% in all cases.

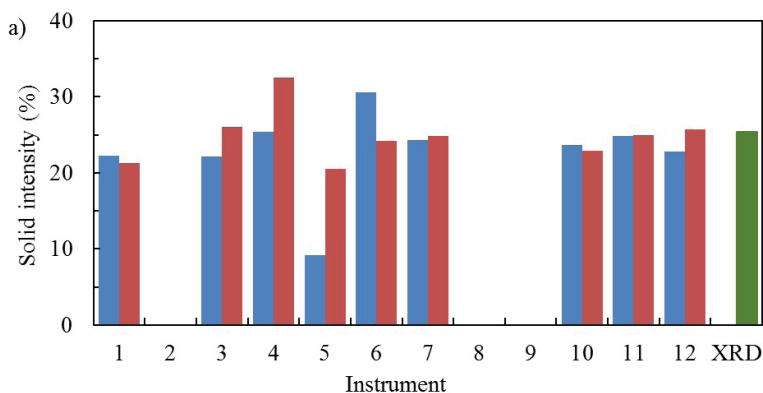


Figure 24: Blue bars: the fractional intensity of the chemically combined water for grey Portland cement paste mixed at $w/c = 0.40$ as measured using solid echo on different instruments. No data indicates that measurements could not be made. Red bars: the fractional intensity corrected for instrumentation variations on the basis of the reference material results. The green bar at the rightmost side is the equivalent result calculated from X-ray diffraction data of a single sample.

Using a reference derived calibration factor

In an attempt to separate instrumentation from sample effects, an instrument-specific correction factor is defined as:

$$\zeta_{sol} = f_{mass}^{sol-ref} / f_{nmr}^{sol-ref} \quad (24)$$

where $f_{mass}^{sol-ref}$ and $f_{nmr}^{sol-ref}$ are the chemically combined water molar fractions of the reference materials for each instrument determined by gravimetry and NMR respectively. The red bars in Figure 24 show the solid echo results of the grey Portland cement multiplied by the correction factor. The average corrected chemically combined water fraction is $24.8 \pm 3.1\%$ for $w/c = 0.40$. Once the data recorded with instruments with a long first τ_q are removed from the analysis (instruments 4 and 5), the average across the remaining data sets is $24.3 \pm 1.6\%$. The percentage calculated from XRD data recorded from one further sample is 25.4%. It should be noted that the XRD analysis is also subject to uncertainty. However, the extent of that uncertainty has not been quantified here.

Possible pitfalls in characterising cement pore water identified by the Round Robin Trial

The Round Robin Trial identified a number of possible pitfalls that lead to errors and uncertainties in quantifying pore water using CPMG analysis. As well as those issues noted in the box “General observations concerning CPMG and reference materials” in the previous section, a number of further issues were identified. These are discussed in the main text. They include:

- Laplace inversion artefacts resulting from low signal to noise ratio or poorly set RF pulses;
- Poor choice of first CPMG τ_1 leading to inaccurate measurement of pore water;
- Variations in sample size;
- Sample temperature and water evaporation.

As before, there are both instrumentation and sample differences that can explain much of the apparent variation between instruments. These are discussed below.

Laplace inversion artefacts. Data recorded with some instruments have a lower signal to noise ratio than is desirable for the inverse Laplace transform. One manifestation of poor signal to noise ratio is poorly resolved peaks in the distribution; for instance, the three peaks merge into two at intermediate relaxation times. Another is the appearance of spurious peaks in the T_2 distribution at times well below the window spanned by the echoes. These are especially apparent if there is an artefact in the intensity of the first few echoes. Such artefacts commonly arises from poor B_1 homogeneity or poorly set pulse flip angles. Possible examples of merged peaks are seen for instruments 2 and 4. Low T_2 artefacts are seen for instruments 3, 6 and 12. Such data needs to be treated with extreme care though it can often still be used if the merged or spurious peaks are understood.

First pulse gap too short or too long. Measurements with instruments 2, 8 and 11 were made with the first τ_1 value more than twice that proposed in the protocol: 64, 88 and 64 μs respectively. With such a long first echo time, the first component of the NMR cement T_2 distribution is either not resolved at all or is poorly differentiated from the next. Along with low signal to noise, this may have contributed to the apparent merging of peaks seen for instrument 2. On the other hand, in the case of instrument 6 the first pulse gap $\tau_1 = 26 \mu\text{s}$ is so short as to allow corruption of the mobile signal by the tail of the solid signal. This may also have contributed to the low T_2 artefact seen for this instrument.

The influence of sample size. Measurements have been carried out using samples of different size designed to fit probes with diameters ranging from 10 mm to 38 mm, almost a factor of 4. The degree of hydration depends critically on the availability

of water. As previously noted, smaller samples are able to draw in water during underwater curing to a much greater extent than larger samples. Also, it is known that larger samples undergo less macroscopic shrinkage than smaller samples^[46] so that the amount of capillary porosity is different. Consequently, the experiments do not always compare like with like. The 10 mm probes and hence samples that can be compared directly, are those for instruments 3, 4, 6, 10 and 12. There are three ~18 mm probes: instruments 1, 7 and 8; two ~25 mm: instruments 5 and 11; one 38 mm: instrument 2; and one of 50 mm, instrument 9, that was not used for cement paste studies.

Sample temperature. Instruments 10 and 11 had a sample space temperature of 40 °C, significantly higher than all the others. Increased temperature potentially changes the relaxation times, and causes an evaporation and redistribution of water within the sample. Heating of the sample in these instruments was evidenced by the condensation of evaporated water near the top of sample tubes and in some cases by the breaking of the glass due to pressure build up.

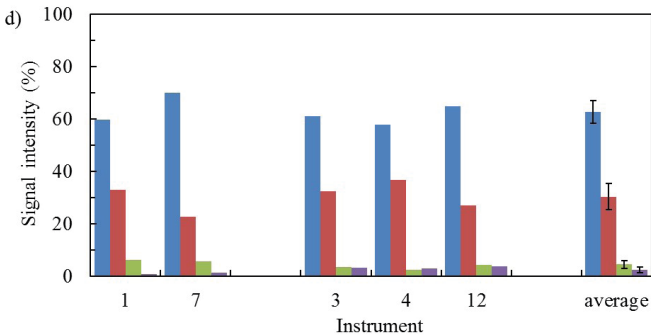
The influence of C₃A. In several instances, the peak around 0.1 ms that has been associated with inter-layer water in C-S-H hydrates in published results of white cement emanating from the Nanocem consortium^[5, 15] is split into two. The Portland cement used here (and indeed the white cement used in subsequent sections of this work) has a significantly higher C₃A fraction than the white cement used in the earlier published studies. It is speculated that this is the primary cause of the effect. The C₃A richer cement has more ettringite and C-A-S-H. Water in nano-channels and interlayer spaces of these hydrates is seen separate from that in the interlayer of C-S-H. For the analysis presented in Figure 25, where this split occurs (instruments 7, 10 and 12), the intensities of the two peaks are combined and the average relaxation time of the hydrates taken. Further investigation was beyond the remit of the Round Robin Trial. We note that Bortolotti *et al.*^[16] have also similar observed multiple “solid” components on the basis of T_1 analysis of other samples.

Constrained multi-exponential fitting. A full inverse Laplace transformation of CPMG data is required when little is known about a sample. However, experience suggests that in many instances sufficient is known to enable a constrained multi-exponential fitting. Multi-exponential fitting of grey Portland cement paste data was performed with T_2 relaxation times set to 110, 387 and 1411 μ s, the average values of the ILT T_2 of five selected data sets – see box “A like-for-like comparison”. The coefficient of determination (R^2) for the majority of the fits is very good: above 0.99. In the case of fits for data measured using 10 mm probes with instruments 3, 4 and 12 the coefficient of determination is somewhat lower as there is an additional long component present in the decay. For those data the fittings were performed including the fourth component at 40 ms.

Very good reproducibility of results is found, Figure 25e. It is seen that many of the instrumentation considerations which limit the inverse Laplace transformation are not so severe as to limit the constrained fitting. The discrepancies of results are 4% - 5% for first and second components and 2% for third component. The average and standard deviation component intensities based on constrained exponential fitting across all participants of Round Robin Trial are $59.2 \pm 4.7\%$, $32.7 \pm 4.4\%$ and $7.2 \pm 1.8\%$.

A like-for-like comparison

In order to make a like-for-like comparison, just five instruments from the Round Robin Trial are chosen: numbers 3, 4, 12 that have 10 mm probes and 1 and 7 that have 18 mm probes. These instruments all operate at or near a frequency of 20 MHz, with comparable measurement parameters and temperature and offered a good signal to noise ratio. The figure below summarises the peak intensity data for just these five.



The fractional intensity of the different pore water fractions: interlayer (blue bars); gel pore (red bars); smaller capillary or inter-hydrate pores (green bars); and filled larger capillary pores (violet bars), for five comparable instruments. The averages and standard deviations are shown on the right.

There is good agreement across the three 10 mm probe instruments taken alone, and still quite good agreement when the 18 mm probes are additionally included. Since grey CEM I is widely used, it is worth considering the variability of the measurements. For these five instruments, the first peak intensity determined by inverse Laplace transformation has a mean and standard deviation of $62.7 \pm 4.3\%$, the second peak $30.4 \pm 5.0\%$, and the third $4.5 \pm 1.4\%$. These averages are presented as the last set of bars in the figure. To compare, these fractions based on constrained exponential fitting are: 62.4 ± 3.7 , 29.7 ± 2.3 and $6.8 \pm 1.3\%$, in excellent agreement with the inverse Laplace transformation analysis.

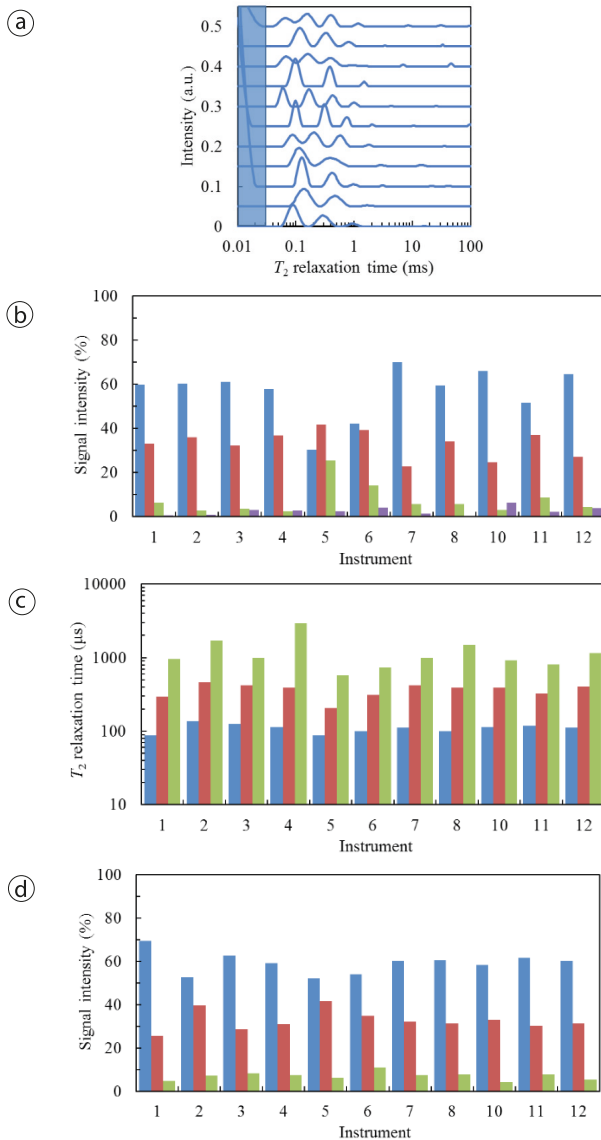


Figure 25: a) The distribution of T_2 from inverse Laplace analysis of CPMG decays for grey Portland cement mixed at $w/c = 0.4$ and cured underwater for 28 days for, from bottom, instruments 1...12 excluding 9. b) The intensity (integrated area) of the three main peaks and the sum of all the remaining peaks presented as 4th component. c) The T_2 of the maximum of the three main peaks. (d) The intensity of the three components derived from multi-exponential fitting with constrained T_2 relaxation times.

Measurement reproducibility

Some of the differences are as likely to be due to measurement reproducibility on any one instrument and sample as they are to subtle differences in the hydration of the cements or differences between instruments. Repeat CPMG measurements were made for the grey Portland cement mixed at $w/c = 0.4$ using instruments 1, 3, 4, 7 and 12 but with just 512 scans. In each case the two sets of data are compared. The estimated reproducibility uncertainty of the peak intensities from the two data sets are as presented in Table 6. In general the variation between measurements on the same instrument is comparable to the scatter between instruments save for instrument 12. A 10% discrepancy for component 1 is, however, unusually poor for instrument 12 for unknown reason(s).

Further results from and discussion of the Round Robin Trial are presented in Appendix F.

Table 6: Reproducibility of repeat measurements

Instrument	Number of scans	1 st component (hydrate interlayer water) (%)	2 nd component (gel pore water) (%)	3 rd component (inter hydrate pore water) (%)
1	512	63.5	30.5	5.3
	1024	59.9	33.1	6.3
	average	61.7 ± 1.8	31.8 ± 1.3	5.8 ± 0.5
3	512	54.5	36.4	6.8
	1024	61.0	32.4	3.5
	average	57.8 ± 3.3	34.4 ± 2.0	5.1 ± 1.7
4	512	50.9	39.0	6.1
	1024	61.0	36.8	2.5
	average	54.4 ± 3.4	37.9 ± 2.0	4.3 ± 1.8
7	512	66.0	24.1	8.3
	1024	70.1	22.7	5.8
	average	68.1 ± 2.1	23.4 ± 0.7	7.0 ± 1.2
12	512	44.2	39.6	11.3
	1024	64.7	27.1	4.2
	average	54.4 ± 10.3	33.3 ± 6.2	8.0 ± 3.7

Differences between white, grey and slag cement?

- In white cement the fraction of water in hydrate interlayer pores is less than that in gel pores, whereas it is greater in grey cement.
- In low C_3A white cement, the chemically combined water in nano-crystalline phases and water in the smallest C-S-H interlayer pores are well resolved. In cement with more typical C_3A content, an extra peak due to *e.g.* zeolitic water in ettringite and/or water in C-A-S-H inter-layer spaces, may appear and potentially complicate the picture.
- Pore water T_2 values are slightly shorter in grey cement compared to white cement, but not so much shorter as to make them overly difficult to measure.
- The T_2^* of water in slag cement is sufficiently short to make it very difficult to separate the water chemically combined in nano-crystalline solid phases from that in pores using the solid echo.

A summary of recommended test parameters and procedures

- A summary of good practice

A summary of good practice

This chapter summarises the key elements of good practice for the NMR characterisation of cement developed in this guide.

NMR frequency. A ^1H frequency in the range 10 - 20 MHz is generally optimum: too high and susceptibility broadening is an issue; too low and the signal to noise ratio is too low.

Magnet homogeneity. A magnetic field homogeneity equivalent to a $^1\text{H } T_2^* \sim 3$ ms is required, even using CPMG, to properly separate hydrate interlayer space, gel pore and capillary pore water.

Samples. Small, centimetre size or less, cement paste samples should be used that are either cured underwater from the very earliest age or sealed. In the former case, if the sample is sufficiently small, it may be assumed that all pores are saturated. However, without using careful gravimetry or knowing the NMR signal immediately after mixing, the total water content due to chemical shrinkage and sorption is unknown. If the latter case, then the total water content is known, but larger pores are expected to be empty of water due to chemical shrinkage.

Magnet/sample temperature. Ideally the samples should be measured at room temperature to avoid evaporation of water. The magnet temperature, which is usually above room temperature, should be maintained sufficiently stable to prevent the NMR frequency shifting during the course of the measurement.

Experiments. As a minimum, the spectrometer should be capable of running a solid echo and a CPMG experiment, preferably log-spaced. Ideally, saturation recovery or inversion recovery is also required in order to ascertain the sample T_1 to set the solid echo and CPMG experiment repetition time. Single pulse FID is required to tune the spectrometer frequency and shim the magnet.

90° pulse length and dead time. The pulse length should be no more than a few microseconds otherwise the pulse bandwidth will not fully excite the crystalline solids. The combination pulse length plus dead time should not exceed 15 μs , ideally 10 – 12 μs otherwise the top of the solid echo cannot be seen at short enough τ_q .

Solid echo. This should be run for a range of τ_q typically between 12 and 55 μs . The first pulse gap should not exceed 15 μs , the shorter the better. About 256 data points with a sampling interval of 1 μs should be captured, starting immediately after the second pulse dead time so as to capture as much of the solid echo peak as possible, including the start of the mobile water FID decay, but not so much of the mobile decay that it is not well represented by the beginning of an exponential decay.

CPMG. The minimum echo time, $2\tau_{min} = \tau_{min}$ required is 60 μs . Too much less, and the first echo catches the tail of the solids; too much more and inter-layer hydrate water is missed. 256 or 512 echoes should be collected, logarithmically spaced and extending out to at least $t_{max} \sim 100\text{ ms}$.

Repetition time. The repetition time between repeat averages of an experiment needs to be at least 3, ideally 5 times the maximum T_1 of any component in the sample. The components with long T_1 are typically capillary pore water and water chemically combined in crystalline solids.

Signal to noise ratio. For inverse Laplace transformation of the data of CPMG data a signal to noise ratio in excess of 500 is recommended. The signal to noise ratio can be significantly less for constrained exponential fitting.

Data analysis. Data should be phased. Solid echoes should be fit to a Gaussian centred on $2\tau_q$ and an exponential decay. The solid echo intensity should be back-extrapolated to zero pulse gap using a second Gaussian to find the proper chemically combined water signal intensity, and the exponential intensity back-extrapolated to find the proper total mobile water signal intensity. The mobile water can be further divided into fractions according to an inverse Laplace transform or multi-exponential fit to the CPMG data. The T_2 of different components reflects the pore size associated with that water component.

Conclusions

- Conclusions
- Acknowledgements

Conclusions

This Guide has described the steps necessary to obtain quantitatively useful and reproducible ^1H NMR measurements of the water contained in different chemical and microstructural environments in cement pastes. From this, the amount of hydrates that have formed, the porosity and the pore size distribution of the paste can be inferred. The Guide has described many of the pitfalls that can lead to irreproducible or inaccurate results. Moreover, the results of a Round Robin Trial of the recommended procedures has been described. The Round Robin Trial has shown the limitations of the measurements, for instance in accurately determining the chemically combined water fraction in slag cements, as well as the accuracy that can be expected, typically $\pm 2\%$ for well-prepared samples with good instrumentation. Finally, suggestions for stable reference materials that mimic the NMR response of cement have been made.

The experienced NMR user will be able to take much of the good practice described here and extend the application of NMR to more complex experiments including: T_1 analysis; $T_1 - T_2$ correlation and $T_2 - T_2$ exchange analysis; measurements of molecular diffusion and q-space microscopy; and to imaging (MRI) since most of these methods include, at heart, pulse sequence elements described in this Guide.

As well as extending to other experiments, the experienced user will also see ways to extend the analysis to more complex cement based materials including mortars and concretes. Some mortars and concretes were indeed included in the Round Robin Trial. However, there were insufficient instruments available that were able to accommodate the larger samples necessary to average over a representative amount of aggregate while still meeting the requirements, *e.g.* for magnet homogeneity or pulse length, to make significant conclusions across multiple instruments possible. Notwithstanding, there is good evidence that useful data from such samples can be obtained.

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References / Further reading

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Appendices

- Appendix A
- Appendix B
- Appendix C
- Appendix D
- Appendix E
- Appendix F

Appendix A: An introduction to NMR

Basic Physics of NMR

Atomic nuclei have a basic property known as “spin”. Spin is associated with intrinsic angular momentum. For many atomic isotopes, the spin is non-zero and in such cases it couples with the nuclear charge in such a way that the nucleus acquires a nuclear magnetic moment, μ . The magnitude of this magnetic moment is given by $\mu = \gamma \hbar [I(I + 1)]^{1/2}$ where γ and I are the magnetogyric ratio and nuclear spin quantum number of the nuclear species under consideration, and $\hbar$ is Planck’s constant, h divided by 2π . Nuclear spin quantum numbers relevant to NMR of cements include:

$I = 1/2$ for ^1H and ^{29}Si , $I = 5/2$ for ^{17}O and ^{27}Al , and $I = 7/2$ for ^{43}Ca .

Other isotopes of these atoms are either not NMR active ($I = 0$) or less naturally abundant.

The energy of a magnetic moment μ in an applied magnetic field $\mathbf{B}_0$ is given by:

$$E = -\mu \cdot \mathbf{B}_0 \quad (\text{A.1})$$

In NMR, by convention, the magnetic field is taken as defining the z -axis of the experimental co-ordinate system. According to the rules of quantum mechanics, the z -component of the spin can take only the values $m_s = I, I - 1, I - 2, \dots - I$. In consequence, the energy is restricted to a discrete set of values or energy levels given by:

$$E = -\gamma \hbar m_s B_0 \quad (\text{A.2})$$

These are known as the nuclear Zeeman energy levels. In the specific case of ^1H , $I = 1/2$, so that:

$$E = \pm \frac{1}{2} \gamma \hbar B_0 \quad (\text{A.3})$$

NMR is associated with transitions between these levels. Since $E = hf$, the frequency, f , of the excitation is given by:

$$f = \gamma / 2\pi B_0 \quad (\text{A.4})$$

According to the alternate classical picture, a magnetic moment in a magnetic field experiences a torque:

$$\Gamma = \boldsymbol{\mu} \times \mathbf{B}_0 \quad (\text{A.5})$$

Equating the torque to the rate of change of angular momentum, $\mathbf{P}$ and recognising that $\boldsymbol{\mu} = \gamma \mathbf{P}$ leads to the classical picture of precession of the magnetic moment about the magnetic field according to which:

$$\mu_x(t) = \mu_T \cos \gamma B_0 t$$

$$\mu_y(t) = \mu_T \sin \gamma B_0 t$$

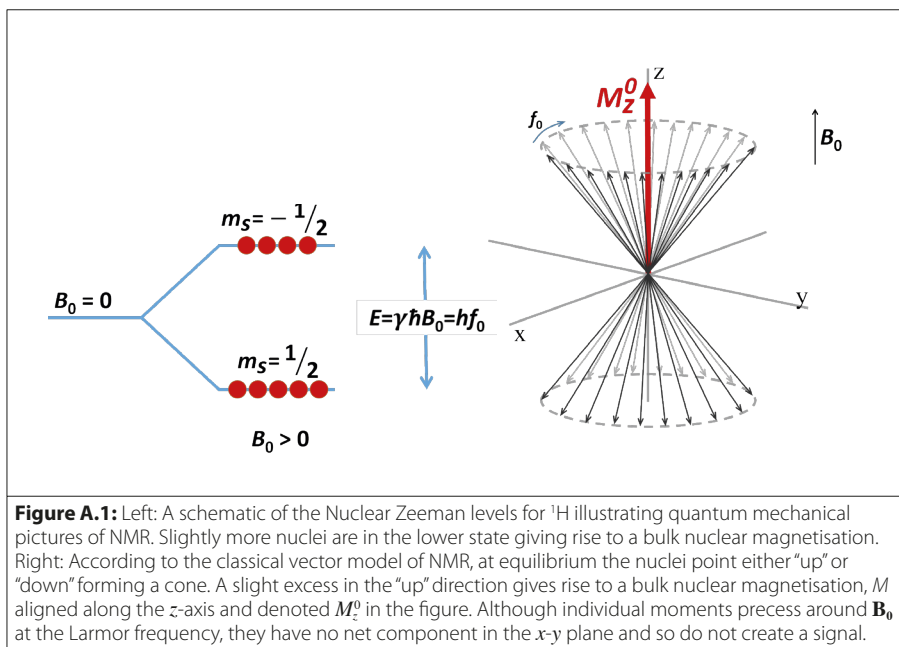
$$\mu_z(t) = \mu_L = (\mu^2 - \mu_T^2)^{1/2} \quad (\text{A.6})$$

for which the precession frequency, f is given by:

$$f = \gamma / 2\pi B_0 \quad (\text{A.7})$$

and where the subscripts T and L refer to the transverse (*i.e.* x - y) plane and longitudinal (*i.e.* z) direction respectively.

This frequency is, of course, the same as that emerging from the quantum picture. Equations A.4 and A.7 are the same and known as the Larmor equation. In both the classical and quantum pictures, one considers an ensemble of nuclei experiencing the same magnetic field. This leads to the concept of a bulk nuclear magnetisation made up of the vector sum of the individual magnetic moments of the individual nuclei. Figure A.1 is a schematic diagram to illustrate the two pictures of NMR: classical precession and quantum excitation.

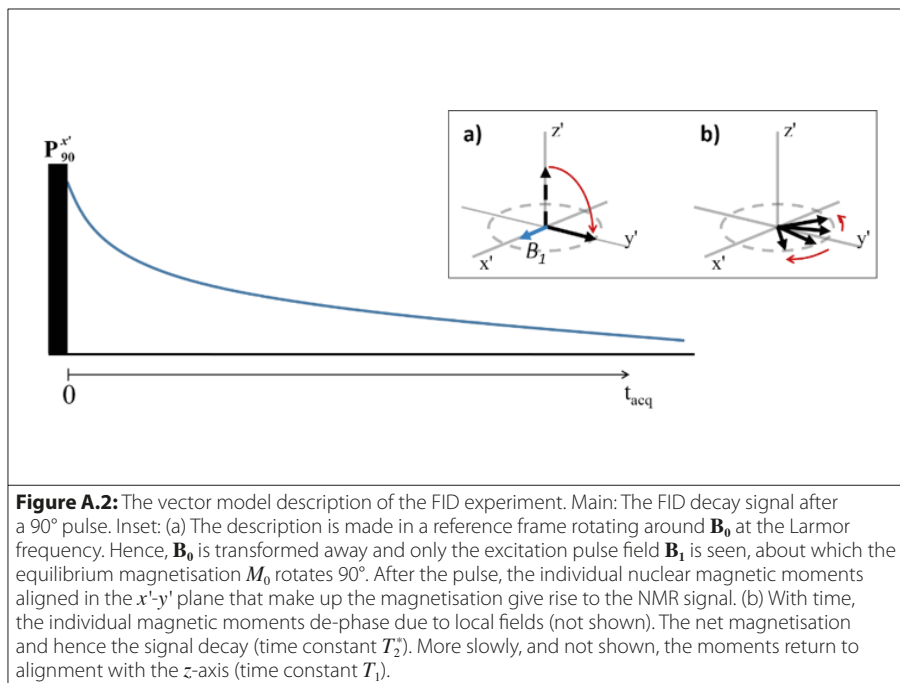


Excitation and the free induction decay, FID

An NMR relaxation experiment consists in placing the sample in a magnetic field. The nuclear magnetic moments that are otherwise randomly oriented rapidly align with or against the magnetic field direction according to the quantum number $m_s = \pm 1/2$. There is a slight preference for the "up", $m_s = +1/2$, direction since it has lower energy. The fraction in the two orientations is determined by the Boltzmann factor. At typical laboratory magnetic field strengths, the excess fraction is about one per million nuclei. Notwithstanding that it is small, this excess creates a bulk nuclear magnetic moment.

The simplest NMR relaxation experiment consists of subjecting the sample to a pulse of radio frequency radiation at the resonant frequency. The pulse is generated by passing an alternating current through a coil of wire around the sample. One way of viewing this pulse is that it excites nuclei from the lower energy state to the higher energy state. The pulse is made to be of sufficient duration as to equalise the populations of the two levels.

The vector model of the FID. The alternate viewpoint is that the radio frequency electromagnetic radiation comprises a magnetic field, $\mathbf{B}_1$, orthogonal to, and rotating at the Larmor frequency about, the primary static field, $\mathbf{B}_0$. In the reference frame rotating with $\mathbf{B}_1$, known in NMR as the rotating reference frame, the static field is transformed to zero and the magnetisation precesses around $\mathbf{B}_1$, aligned say, along the x' axis, at a frequency $f_1 = \gamma / 2\pi B_0$ towards the y' axis. The pulse of $\mathbf{B}_1$ magnetic field is left on for a sufficient time to rotate the magnetisation by 90° , as shown in inset (a) of Figure A.2. Hence it is commonly referred to as a 90° , $\pi/2$ or P_{90} excitation pulse.



Following the pulse, the macroscopic nuclear magnetisation is left lying in the plane transverse to the main field. The magnetisation now starts to precess about $\mathbf{B}_0$ according to Equation A.6. In doing so, it induces an alternating current at the Larmor frequency in the coil around the sample. This current, amplified and demodulated much as a conventional radio would amplify and demodulate radio broadcasts, is the origin of the NMR signal. Of course, in the rotating frame, the magnetisation is static along the y' axis. The signal persists so long as the individual magnetic moments of all the ^1H in the sample precess in phase. In practice, they all experience slightly different magnetic fields due to magnetic interactions between themselves and because the applied field is never perfectly homogeneous. For this reason, they lose coherence,

Figure A.2 inset (b). That is, some precess faster than others. Their vector sum in the transverse plane decreases and so the signal amplitude decreases, approximately exponentially, Figure A.2 (main). The decaying signal is known as the *free induction decay* or FID. The characteristic signal decay time is commonly referred to as T_2^* as explained in the next section. However, even when the signal is completely gone, the nuclei have not necessarily returned to equilibrium, aligned with, or against, the magnetic field $\mathbf{B}_0$. They have only lost “coherence” *within* their respective energy levels. To return fully to equilibrium requires energy to move nuclei between the energy levels. This energy comes from lattice vibrations and occurs on a timescale T_1 . Only then can the experiment be repeated.

The Hahn echo and CPMG

Figure A.3 shows the formation of a Hahn or spin echo according to the vector model of NMR. The initial 90° pulse, (a), is followed at time τ by a 180° pulse along an orthogonal axis in the rotating frame, (c). The 180° pulse serves to reverse the precession angle of the nuclei in the x' - y' plane. If the origin of the local field is magnetic field inhomogeneity, then the nuclei continue to precess in the same direction, (d), with the result that they come back into phase at time 2τ , (e). A Hahn or spin echo forms. T_2^{AB} relaxation is overcome. However, de-phasing due to internuclear interactions is not reversed, so the echo is attenuated by true T_2 relaxation.

Repeated application of 180° pulses at $\tau, 3\tau, 5\tau$, etc. yields repeated echoes at $2\tau, 4\tau, 6\tau$, etc. This is the CPMG experiment.

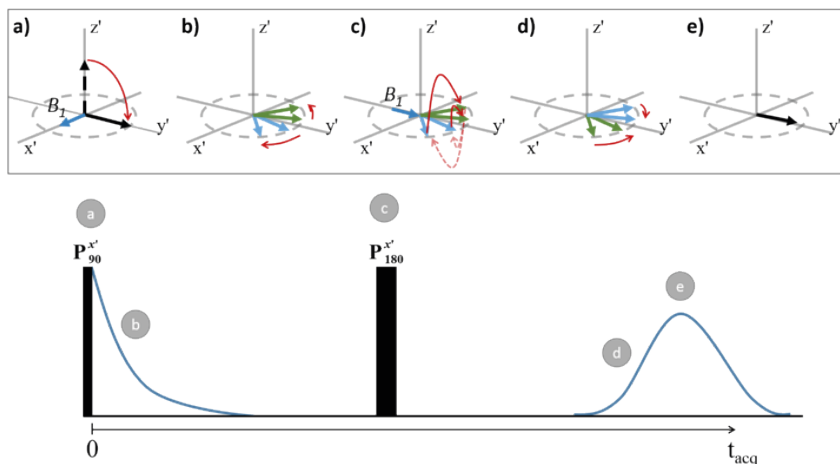


Figure A.3: The vector model description of the Hahn experiment that starts with excitation, (a) and the FID, (b). Thereafter, a 180° pulse is applied 90° out of phase with the first pulse (c). It causes nuclei to reverse their phase angle in the $x'-y'$ frame. They continue to rotate about local fields. If those fields are due to magnet inhomogeneities then each nucleus continues to rotate in the same direction, (d), and so they come back into phase and a full echo is seen, (e). However, if the local field is due to a neighbour nucleus then this interaction is "reversed" and not re-phased. In this way T_2 and T_2^* relaxations are separated.

Appendix B: The inverse Laplace transformation and exponential curve-fitting

Multi-exponential fitting

In the case of multi-component exponential fitting, a distribution of n T_2 components is assumed and the decay is written as:

$$I_{liq}(t) = \sum_{i=1}^n I_i \exp(-t/T_{2i}) \quad (B.1)$$

where I_i is the intensity fraction, T_{2i} is the T_2 relaxation time of i^{th} component of the distribution, and t is time counted from the 90° pulse of the CPMG experiment. The multi-modal distribution for T_2 relaxation can be solved using pre-defined least square fitting procedures such as that incorporated in Origin® or by creating such a routine using, for instance, Matlab® or the Solver function available for Excel®. However, applying these routines for analysis may be difficult as the obtained intensities and relaxation times depend hugely on the supposed number of components and more especially on their initial guess values. For this reason it is often beneficial to constrain the fitting, for instance by specifying the T_2 values – or at least their ratios – based on prior knowledge. Constraining the T_2 ratios is justified on the grounds that while the surface relaxivity of cements may depend hugely on the density of paramagnetic impurities in the cement, the ratio of pore sizes tends to be more limited. For engineering applications associated with coarse characterisation of construction materials in the field, this approach may be deemed adequate. The experience of the authors is that constraining to a four component fit where the shortest three relaxation times are held in the ratio 1 : 3 : 9 to 1 : 4 : 16 and the fourth is fixed long often suffices. Then just the four amplitudes and shortest time are left to float.

A variation of multi-component fitting is exponential stripping. Here the data towards the end of the decay, at long times only, are fitted to a single exponential decay. This fitting is subtracted from the data and the next longest decay in the data similarly fitted. An iterative process is followed until all components are found. A practical problem using this method for cements is that the data cut-off time for a component with T_{2i} should be greater than three to five times T_{2i-1} where $T_{2i} > T_{2i-1}$. Since it is generally found for cements that $T_{2i} \approx 3T_{2i-1}$ where $i = 2, 3$, this means that a large fraction of the i^{th} component has already decayed before it can be fitted.

Inverse Laplace Transform

The relaxation time distribution for T_2 is better expressed as

$$I_{liq}(t) = \int P(T_2) \exp(-t/T_2) dT_2 \quad (B.2)$$

where $P(T_2)$ is the relaxation time probability distribution function. An inverse Laplace transformation (ILT) is used to find P , knowing the signal intensity.

Strictly, analysis of data recorded at discrete times involves a discrete ILT which actually reduces the fit to a summation over a large number of components. Moreover, real data contain a contribution from noise, $\varepsilon(t)$. Laplace inversion of discrete data containing noise is known to be an ill-posed problem. Various algorithms have been proposed, ^[49, 50, 51, 55, 56]. Many NMR spectrometers come with an ILT algorithm preprogrammed. ILT routines generally require the Kernel function to be specified. For CPMG data to measure T_2 it is:

$$\exp(-t/T_2) \quad (B.3)$$

whereas for T_1 it is:

$$1 - \alpha \exp(-t/T_1) \quad (B.4)$$

where $\alpha = 1$ for saturation-recovery and $\alpha = 2$ for inversion-recovery.

Most algorithms require setting of a “regularisation parameter” that smooths the data. The algorithms often include methods to optimise this parameter which are usually based on the concept of not “over fitting” the data with too many (unphysical) modes in the distribution. If the parameter is poorly set, then peaks in the T_2 distribution corresponding to different pore size modes are either not resolved (that is they are merged) or conversely appear with unrealistically low width. Notwithstanding this, a property of some inversion algorithms is that the integrated area of peaks is relatively insensitive to their apparent width so that the relative intensities of different modes based on their areas can be reasonably estimated.

Appendix C provides computer generated test data sets on which fitting procedures and algorithms can be tested.

Appendix C: Test data sets

The tables in this appendix offer a series of computer generated data sets (A, B, C ... S) that are typical of CPMG results with 1, 2 and 3 T_2 components and with different signal to noise levels and different simulated artefacts. They are designed to allow the reader to test the robustness of their own implementations of exponential fitting and inverse Laplace transformation.

A description of each set and the generating equations are given in the following tables.

Table C1: One component data sets					
Echo time (ms)	A	B	C	D	E
0.1	0.9355	0.9350	0.9303	0.9455	0.9445
0.2	0.8752	0.8744	0.8670	0.8852	0.8835
0.3	0.8187	0.8191	0.8229	0.8287	0.8296
0.4	0.7659	0.7642	0.7482	0.7759	0.7724
0.5	0.7165	0.7172	0.7232	0.7265	0.7279
0.6	0.6703	0.6689	0.6562	0.6803	0.6775
0.7	0.6271	0.6288	0.6441	0.6371	0.6405
0.8	0.5866	0.5853	0.5733	0.5966	0.5940
0.9	0.5488	0.5511	0.5714	0.5588	0.5633
1.0	0.5134	0.5147	0.5264	0.5234	0.5260
1.1	0.4803	0.4778	0.4555	0.4903	0.4853
1.2	0.4493	0.4491	0.4469	0.4593	0.4589
1.3	0.4204	0.4175	0.3916	0.4304	0.4246
1.4	0.3932	0.3925	0.3860	0.4032	0.4018
1.5	0.3679	0.3657	0.3465	0.3779	0.3736
1.6	0.3442	0.3435	0.3375	0.3542	0.3528
1.7	0.3220	0.3243	0.3455	0.3320	0.3367
1.8	0.3012	0.3014	0.3031	0.3112	0.3116
1.9	0.2818	0.2816	0.2803	0.2918	0.2915
2.0	0.2636	0.2635	0.2625	0.2736	0.2734
2.1	0.2466	0.2455	0.2358	0.2566	0.2544
2.2	0.2307	0.2313	0.2366	0.2407	0.2419
2.3	0.2158	0.2128	0.1860	0.2258	0.2199
2.4	0.2019	0.2029	0.2121	0.2119	0.2139
2.5	0.1889	0.1912	0.2117	0.1989	0.2034
2.6	0.1767	0.1782	0.1913	0.1867	0.1896
2.7	0.1653	0.1641	0.1534	0.1753	0.1729
2.8	0.1546	0.1547	0.1551	0.1646	0.1647
2.9	0.1447	0.1446	0.1437	0.1547	0.1545
3.0	0.1353	0.1340	0.1222	0.1453	0.1427

3.1	0.1266	0.1290	0.1503	0.1366	0.1413
3.2	0.1184	0.1177	0.1113	0.1284	0.1270
3.3	0.1108	0.1109	0.1116	0.1208	0.1210
3.4	0.1037	0.1026	0.0932	0.1137	0.1116
3.5	0.0970	0.0953	0.0807	0.1070	0.1037
3.6	0.0907	0.0898	0.0812	0.1007	0.0988
3.7	0.0849	0.0862	0.0982	0.0949	0.0975
3.8	0.0794	0.0809	0.0940	0.0894	0.0923
3.9	0.0743	0.0730	0.0615	0.0843	0.0817
4.0	0.0695	0.0702	0.0768	0.0795	0.0809
4.1	0.0650	0.0664	0.0791	0.0750	0.0778
4.2	0.0608	0.0609	0.0619	0.0708	0.0710
4.3	0.0569	0.0597	0.0852	0.0669	0.0725
4.4	0.0532	0.0527	0.0476	0.0632	0.0621
4.5	0.0498	0.0527	0.0792	0.0598	0.0657
4.6	0.0466	0.0413	-0.0064	0.0566	0.0460
4.7	0.0436	0.0494	0.1019	0.0536	0.0652
4.8	0.0408	0.0445	0.0785	0.0508	0.0583
4.9	0.0381	0.0363	0.0198	0.0481	0.0445
5.0	0.0357	0.0352	0.0308	0.0457	0.0447
5.1	0.0334	0.0351	0.0508	0.0434	0.0469
5.2	0.0312	0.0331	0.0497	0.0412	0.0449
5.3	0.0292	0.0302	0.0391	0.0392	0.0412
5.4	0.0273	0.0310	0.0643	0.0373	0.0447
5.5	0.0256	0.0196	-0.0336	0.0356	0.0237
5.6	0.0239	0.0243	0.0276	0.0339	0.0346
5.7	0.0224	0.0209	0.0079	0.0324	0.0295
5.8	0.0209	0.0198	0.0097	0.0309	0.0287
5.9	0.0196	0.0193	0.0166	0.0296	0.0290
6.0	0.0183	0.0188	0.0228	0.0283	0.0292
6.1	0.0171	0.0168	0.0138	0.0271	0.0265
6.2	0.0160	0.0156	0.0121	0.0260	0.0252
6.3	0.0150	0.0152	0.0171	0.0250	0.0254
6.4	0.0140	0.0136	0.0096	0.0240	0.0231
6.5	0.0131	0.0126	0.0079	0.0231	0.0226
6.6	0.0123	0.0115	0.0041	0.0223	0.0215
6.7	0.0115	0.0119	0.0157	0.0215	0.0219
6.8	0.0107	0.0090	-0.0070	0.0207	0.0190
6.9	0.0101	0.0107	0.0168	0.0201	0.0207
7.0	0.0094	0.0080	-0.0048	0.0194	0.0180
7.1	0.0088	0.0105	0.0258	0.0188	0.0205
7.2	0.0082	0.0069	-0.0051	0.0182	0.0169
7.3	0.0077	0.0100	0.0303	0.0177	0.200
7.4	0.0072	0.0085	0.0201	0.0172	0.0185
7.5	0.0067	0.0043	-0.0181	0.0167	0.0143

Table C2: Two-component data sets

Echo time (ms)	F	G	H	I	J	K	L
0.1	0.8730	0.8704	0.8830	0.7655	0.7629	0.7755	0.7729
0.2	0.7665	0.7624	0.7765	0.8435	0.8394	0.8535	0.8494
0.3	0.6767	0.6787	0.6867	0.6215	0.6236	0.6315	0.6336
0.4	0.6003	0.5915	0.6103	0.6399	0.6310	0.6499	0.6410
0.5	0.5350	0.5383	0.5450	0.5067	0.5100	0.5167	0.5200
0.6	0.4787	0.4717	0.4887	0.4990	0.4920	0.5090	0.5020
0.7	0.4299	0.4384	0.4399	0.4154	0.4239	0.4254	0.4339
0.8	0.3874	0.3807	0.3974	0.3978	0.3912	0.4078	0.4012
0.9	0.3500	0.3613	0.3600	0.3426	0.3539	0.3526	0.3639
1.0	0.3171	0.3236	0.3271	0.3224	0.3289	0.3324	0.3389
1.1	0.2879	0.2755	0.2979	0.2840	0.2716	0.2940	0.2816
1.2	0.2618	0.2607	0.2718	0.2646	0.2634	0.2746	0.2734
1.3	0.2386	0.2242	0.2486	0.2366	0.2222	0.2466	0.2322
1.4	0.2177	0.2140	0.2277	0.2191	0.2154	0.2291	0.2254
1.5	0.1988	0.1882	0.2088	0.1978	0.1871	0.2078	0.1971
1.6	0.1818	0.1785	0.1918	0.1826	0.1792	0.1926	0.1892
1.7	0.1664	0.1782	0.1764	0.1659	0.1777	0.1759	0.1877
1.8	0.1525	0.1534	0.1625	0.1528	0.1538	0.1628	0.1638
1.9	0.1397	0.1390	0.1497	0.1395	0.1387	0.1495	0.1487
2.0	0.1282	0.1276	0.1382	0.1284	0.1278	0.1384	0.1378
2.1	0.1176	0.1122	0.1276	0.1175	0.1120	0.1275	0.1220
2.2	0.1079	0.1109	0.1179	0.1080	0.1110	0.1180	0.1210
2.3	0.0991	0.0842	0.1091	0.0991	0.0842	0.1091	0.0942
2.4	0.0910	0.0962	0.1010	0.0911	0.0962	0.1011	0.1062
2.5	0.0837	0.0950	0.0937	0.0836	0.0950	0.0936	0.1050
2.6	0.0769	0.0842	0.0869	0.0769	0.0842	0.0869	0.0942
2.7	0.0707	0.0647	0.0807	0.0706	0.0647	0.0806	0.0747
2.8	0.0650	0.0652	0.0750	0.0650	0.0652	0.0750	0.0752
2.9	0.0597	0.0593	0.0697	0.0597	0.0592	0.0697	0.0692
3.0	0.0549	0.0483	0.0649	0.0549	0.0484	0.0649	0.0584
3.1	0.0505	0.0623	0.0605	0.0505	0.0623	0.0605	0.0723
3.2	0.0464	0.0429	0.0564	0.0464	0.0429	0.0564	0.0529
3.3	0.0427	0.0431	0.0527	0.0427	0.0431	0.0527	0.0531
3.4	0.0393	0.0340	0.0493	0.0393	0.0340	0.0493	0.0440
3.5	0.0361	0.0280	0.0461	0.0361	0.0280	0.0461	0.0380
3.6	0.0332	0.0285	0.0432	0.0332	0.0285	0.0432	0.0385
3.7	0.0306	0.0372	0.0406	0.0306	0.0372	0.0406	0.0472
3.8	0.0281	0.0354	0.0381	0.0281	0.0354	0.0381	0.0454
3.9	0.0259	0.0195	0.0359	0.0259	0.0195	0.0359	0.0295
4.0	0.0238	0.0275	0.0338	0.0238	0.0275	0.0338	0.0375
4.1	0.0219	0.0289	0.0319	0.0219	0.0289	0.0319	0.0389

4.2	0.0201	0.0207	0.0301	0.0201	0.0207	0.0301	0.0307
4.3	0.0185	0.0327	0.0285	0.0185	0.0327	0.0285	0.0427
4.4	0.0170	0.0142	0.0270	0.0170	0.0142	0.0270	0.0242
4.5	0.0157	0.0304	0.0257	0.0157	0.0304	0.0257	0.0404
4.6	0.0144	-0.0120	0.0244	0.0144	-0.0120	0.0244	-0.0020
4.7	0.0133	0.0425	0.0233	0.0133	0.0425	0.0233	0.0525
4.8	0.0122	0.0311	0.0222	0.0122	0.0311	0.0222	0.0411
4.9	0.0112	0.0021	0.0212	0.0112	0.0021	0.0212	0.0121
5.0	0.0103	0.0079	0.0203	0.0103	0.0079	0.0203	0.0179
5.1	0.0095	0.0182	0.0195	0.0095	0.0182	0.0195	0.0282
5.2	0.0087	0.0180	0.0187	0.0087	0.0180	0.0187	0.0280
5.3	0.0081	0.0130	0.0181	0.0081	0.0130	0.0181	0.0230
5.4	0.0074	0.0259	0.0174	0.0074	0.0259	0.0174	0.0359
5.5	0.0068	-0.0228	0.0168	0.0068	-0.0228	0.0168	-0.0128
5.6	0.0063	0.0081	0.0163	0.0063	0.0081	0.0163	0.0181
5.7	0.0058	-0.0014	0.0158	0.0058	-0.0014	0.0158	0.0086
5.8	0.0053	-0.0003	0.0153	0.0053	-0.0003	0.0153	0.0097
5.9	0.0049	0.0034	0.0149	0.0049	0.0034	0.0149	0.0134
6.0	0.0045	0.0067	0.0145	0.0045	0.0067	0.0145	0.0167
6.1	0.0041	0.0025	0.0141	0.0041	0.0025	0.0141	0.0125
6.2	0.0038	0.0018	0.0138	0.0038	0.0018	0.0138	0.0118
6.3	0.0035	0.0045	0.0135	0.0035	0.0045	0.0135	0.0145
6.4	0.0032	0.0010	0.0132	0.0032	0.0010	0.0132	0.0110

Table C3: Three-component data sets

Echo time (ms)	M	N	O	P	Q	R	S
0.066	0.8217	0.8209	0.8317	0.7638	0.7630	0.7738	0.7730
0.101	0.7502	0.7506	0.7602	0.6431	0.6435	0.6531	0.6535
0.137	0.6886	0.6868	0.6986	0.6507	0.6489	0.6607	0.6589
0.174	0.6349	0.6356	0.6449	0.6925	0.6932	0.7025	0.7032
0.212	0.5878	0.5864	0.5978	0.6563	0.6549	0.6663	0.6649
0.252	0.5460	0.5477	0.5560	0.5427	0.5444	0.5527	0.5544
0.292	0.5087	0.5073	0.5187	0.4537	0.4524	0.4637	0.4624
0.334	0.4750	0.4772	0.4850	0.4511	0.4534	0.4611	0.4634
0.377	0.4443	0.4456	0.4543	0.4763	0.4775	0.4863	0.4875
0.421	0.4161	0.4137	0.4261	0.4451	0.4426	0.4551	0.4526
0.467	0.3902	0.3900	0.4002	0.3742	0.3740	0.3842	0.3840
0.514	0.3662	0.3633	0.3762	0.3417	0.3388	0.3517	0.3488
0.562	0.3438	0.3431	0.3538	0.3525	0.3518	0.3625	0.3618
0.612	0.3230	0.3208	0.3330	0.3411	0.3389	0.3511	0.3489
0.663	0.3035	0.3028	0.3135	0.2967	0.2961	0.3067	0.3061
0.716	0.2852	0.2876	0.2952	0.2732	0.2756	0.2832	0.2856
0.771	0.2681	0.2683	0.2781	0.2751	0.2753	0.2851	0.2853
0.827	0.2521	0.2519	0.2621	0.2584	0.2582	0.2684	0.2682
0.885	0.2370	0.2369	0.2470	0.2300	0.2299	0.2400	0.2399
0.944	0.2229	0.2218	0.2329	0.2218	0.2207	0.2318	0.2307
1.006	0.2097	0.2103	0.2197	0.2149	0.2154	0.2249	0.2254
1.069	0.1973	0.1943	0.2073	0.1949	0.1919	0.2049	0.2019
1.134	0.1857	0.1867	0.1957	0.1840	0.1850	0.1940	0.1950
1.201	0.1748	0.1770	0.1848	0.1775	0.1798	0.1875	0.1898
1.270	0.1645	0.1660	0.1745	0.1633	0.1647	0.1733	0.1747
1.341	0.1550	0.1538	0.1650	0.1545	0.1533	0.1645	0.1633
1.414	0.1460	0.1460	0.1560	0.1472	0.1472	0.1572	0.1572
1.489	0.1375	0.1375	0.1475	0.1366	0.1365	0.1466	0.1465
1.567	0.1296	0.1283	0.1396	0.1300	0.1287	0.1400	0.1387
1.647	0.1222	0.1246	0.1322	0.1222	0.1246	0.1322	0.1346
1.730	0.1152	0.1145	0.1252	0.1149	0.1142	0.1249	0.1242
1.814	0.1086	0.1087	0.1186	0.1089	0.1090	0.1189	0.1190
1.902	0.1024	0.1013	0.1124	0.1021	0.1010	0.1121	0.1110
1.992	0.0965	0.0948	0.1065	0.0967	0.0950	0.1067	0.1050
2.085	0.0909	0.0900	0.1009	0.0908	0.0898	0.1008	0.0998
2.180	0.0856	0.0870	0.0956	0.0857	0.0871	0.0957	0.0971
2.279	0.0806	0.0821	0.0906	0.0806	0.0820	0.0906	0.0920
2.380	0.0759	0.0746	0.0859	0.0759	0.0747	0.0859	0.0847
2.484	0.0714	0.0721	0.0814	0.0713	0.0721	0.0813	0.0821
2.592	0.0671	0.0685	0.0771	0.0671	0.0685	0.0771	0.0785
2.703	0.0630	0.0631	0.0730	0.0630	0.0631	0.0730	0.0731

2.817	0.0591	0.0619	0.0691	0.0591	0.0619	0.0691	0.0719
2.934	0.0553	0.0548	0.0653	0.0553	0.0548	0.0653	0.0648
3.055	0.0518	0.0547	0.0618	0.0518	0.0547	0.0618	0.0647
3.180	0.0484	0.0431	0.0584	0.0484	0.0431	0.0584	0.0531
3.308	0.0451	0.0510	0.0551	0.0451	0.0510	0.0551	0.0610
3.440	0.0420	0.0458	0.0520	0.0420	0.0458	0.0520	0.0558
3.577	0.0391	0.0373	0.0491	0.0391	0.0373	0.0491	0.0473
3.717	0.0363	0.0358	0.0463	0.0363	0.0358	0.0463	0.0458
3.861	0.0336	0.0354	0.0436	0.0336	0.0354	0.0436	0.0454
4.010	0.0311	0.0329	0.0411	0.0311	0.0329	0.0411	0.0429
4.163	0.0287	0.0297	0.0387	0.0287	0.0297	0.0387	0.0397
4.321	0.0264	0.0301	0.0364	0.0264	0.0301	0.0364	0.0401
4.484	0.0242	0.0183	0.0342	0.0242	0.0183	0.0342	0.0283
4.651	0.0222	0.0226	0.0322	0.0222	0.0226	0.0322	0.0326
4.824	0.0203	0.0188	0.0303	0.0203	0.0188	0.0303	0.0288
5.002	0.0185	0.0174	0.0285	0.0185	0.0174	0.0285	0.0274
5.185	0.0168	0.0165	0.0268	0.0168	0.0165	0.0268	0.0265
5.373	0.0152	0.0157	0.0252	0.0152	0.0157	0.0252	0.0257
5.567	0.0138	0.0134	0.0238	0.0138	0.0134	0.0238	0.0234
5.767	0.0124	0.0120	0.0224	0.0124	0.0120	0.0224	0.0220
5.973	0.0111	0.0113	0.0211	0.0111	0.0113	0.0211	0.0213
6.186	0.0100	0.0095	0.0200	0.0100	0.0095	0.0200	0.0195
6.404	0.0089	0.0089	0.0189	0.0089	0.0089	0.0189	0.0189
6.629	0.0079	0.0075	0.0179	0.0079	0.0075	0.0179	0.0175
6.861	0.0070	0.0079	0.0170	0.0070	0.0079	0.0170	0.0179
7.100	0.0062	0.0058	0.0162	0.0062	0.0058	0.0162	0.0158
7.346	0.0054	0.0058	0.0154	0.0054	0.0058	0.0154	0.0158
7.599	0.0048	0.0064	0.0148	0.0048	0.0064	0.0148	0.0164
7.860	0.0042	0.0044	0.0142	0.0042	0.0044	0.0142	0.0144
8.129	0.0036	0.0001	0.0136	0.0036	0.0001	0.0136	0.0101
8.406	0.0031	0.0059	0.0131	0.0031	0.0059	0.0131	0.0159
8.691	0.0027	0.0002	0.0127	0.0027	0.0002	0.0127	0.0102
8.985	0.0023	-0.0004	0.0123	0.0023	-0.0004	0.0123	0.0096
9.287	0.0020	0.0045	0.0120	0.0020	0.0045	0.0120	0.0145
9.599	0.0017	0.0077	0.0117	0.0017	0.0077	0.0117	0.0177
9.920	0.0014	0.0002	0.0114	0.0014	0.0002	0.0114	0.0102
10.251	0.0012	0.0002	0.0112	0.0012	0.0002	0.0112	0.0102
10.591	0.0010	0.0018	0.0110	0.0010	0.0018	0.0110	0.0118
10.942	0.0008	-0.0007	0.0108	0.0008	-0.0007	0.0108	0.0093
11.303	0.0007	-0.0030	0.0107	0.0007	-0.0030	0.0107	0.0070
11.675	0.0006	0.0011	0.0106	0.0006	0.0011	0.0106	0.0111
12.058	0.0005	0.0037	0.0105	0.0005	0.0037	0.0105	0.0137
12.453	0.0004	0.0012	0.0104	0.0004	0.0012	0.0104	0.0112
12.860	0.0003	0.0010	0.0103	0.0003	0.0010	0.0103	0.0110
13.279	0.0002	-0.0001	0.0102	0.0002	-0.0001	0.0102	0.0099
13.710	0.0002	-0.0021	0.0102	0.0002	-0.0021	0.0102	0.0079

14.154	0.0002	-0.0009	0.0102	0.0002	-0.0009	0.0102	0.0091
14.612	0.0001	0.0001	0.0101	0.0001	0.0001	0.0101	0.0101
15.083	0.0001	-0.0001	0.0101	0.0001	-0.0001	0.0101	0.0099
15.569	0.0001	-0.0013	0.0101	0.0001	-0.0013	0.0101	0.0087
16.069	0.0001	0.0012	0.0101	0.0001	0.0012	0.0101	0.0112
16.584	0.0000	-0.0013	0.0100	0.0000	-0.0013	0.0100	0.0087
17.114	0.0000	0.0020	0.0100	0.0000	0.0020	0.0100	0.0120
17.661	0.0000	0.0015	0.0100	0.0000	0.0015	0.0100	0.0115
18.223	0.0000	-0.0019	0.0100	0.0000	-0.0019	0.0100	0.0081
18.803	0.0000	-0.0032	0.0100	0.0000	-0.0032	0.0100	0.0068
19.400	0.0000	-0.0017	0.0100	0.0000	-0.0017	0.0100	0.0083
20.015	0.0000	0.0001	0.0100	0.0000	0.0001	0.0100	0.0101
20.649	0.0000	-0.0002	0.0100	0.0000	-0.0002	0.0100	0.0098
21.301	0.0000	0.0002	0.0100	0.0000	0.0002	0.0100	0.0102
21.973	0.0000	-0.0034	0.0100	0.0000	-0.0034	0.0100	0.0066
22.665	0.0000	-0.0033	0.0100	0.0000	-0.0033	0.0100	0.0067
23.378	0.0000	-0.0009	0.0100	0.0000	-0.0009	0.0100	0.0091
24.113	0.0000	0.0010	0.0100	0.0000	0.0010	0.0100	0.0110
24.869	0.0000	-0.0017	0.0100	0.0000	-0.0017	0.0100	0.0083
25.648	0.0000	0.0015	0.0100	0.0000	0.0015	0.0100	0.0115
26.450	0.0000	0.0011	0.0100	0.0000	0.0011	0.0100	0.0111
27.277	0.0000	0.0029	0.0100	0.0000	0.0029	0.0100	0.0129
28.128	0.0000	0.0023	0.0100	0.0000	0.0023	0.0100	0.0123
29.005	0.0000	-0.0038	0.0100	0.0000	-0.0038	0.0100	0.0062
29.908	0.0000	-0.0009	0.0100	0.0000	-0.0009	0.0100	0.0091
30.839	0.0000	0.0014	0.0100	0.0000	0.0014	0.0100	0.0114
31.797	0.0000	0.0013	0.0100	0.0000	0.0013	0.0100	0.0113
32.784	0.0000	0.0008	0.0100	0.0000	0.0008	0.0100	0.0108
33.800	0.0000	0.0003	0.0100	0.0000	0.0003	0.0100	0.0103
34.847	0.0000	-0.0008	0.0100	0.0000	-0.0008	0.0100	0.0092
35.925	0.0000	0.0048	0.0100	0.0000	0.0048	0.0100	0.0148
37.036	0.0000	0.0007	0.0100	0.0000	0.0007	0.0100	0.0107
38.180	0.0000	0.0019	0.0100	0.0000	0.0019	0.0100	0.0119
39.359	0.0000	0.0007	0.0100	0.0000	0.0007	0.0100	0.0107
40.572	0.0000	-0.0019	0.0100	0.0000	-0.0019	0.0100	0.0081
41.823	0.0000	0.0054	0.0100	0.0000	0.0054	0.0100	0.0154
43.110	0.0000	-0.0003	0.0100	0.0000	-0.0003	0.0100	0.0097
44.437	0.0000	0.0010	0.0100	0.0000	0.0010	0.0100	0.0110
45.803	0.0000	0.0015	0.0100	0.0000	0.0015	0.0100	0.0115
47.210	0.0000	0.0006	0.0100	0.0000	0.0006	0.0100	0.0106
47.242	0.0000	0.0006	0.0100	0.0000	0.0006	0.0100	0.0106

Table C4: Test data set descriptors. R^σ is a random number with Gaussian distribution, mean zero and standard deviation σ

Data set	Descriptor	Formula
Single exponential decays, linearly spaced echoes. $\tau = 50 \mu\text{s}$		
A	Decay	$M(t) = M_A(t) = \exp(-t/1.5)$
B	Decay + 0.2% noise	$M(t) = M_A(t) + R^{0.002}$
C	Decay + 2% noise	$M(t) = M_A(t) + R^{0.02}$
D	Decay + 1% baseline	$M(t) = M_A(t) + 0.01$
E	Decay + 0.2% noise + 1% baseline	$M(t) = M_A(t) + R^{0.002} + 0.01$
Two-component exponential decays, linearly spaced echoes. $\tau = 50 \mu\text{s}$		
F	Decay	$T_2 = 0.4 \text{ ms}; I_1 = 1/3; T_2 = 1.2 \text{ ms}; I_2 = 2/3;$ $M(t) = M_F(t) = 1/3 \exp(-t/0.4) + 2/3 \exp(-t/1.2)$
G	Decay + 1% noise	$M(t) = M_F(t) + R^{0.01}$
H	Decay + 1% baseline	$M(t) = M_F(t) + 0.01$
I	Decay + flip angle artefacts	$M(t) = M_F(t) + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
J	Decay + 1% noise + flip angle artefacts	$M(t) = M_F(t) + R^{0.01} + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
K	Decay + 1% baseline + flip angle artefacts	$M(t) = M_F(t) + 0.01 + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
L	Decay + 1% noise + 1% baseline + flip angle artefacts	$M(t) = M_F(t) + R^{0.01} + 0.01 + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
Three-component exponential decays, log-spaced echoes. $\tau = 33 \mu\text{s}$		
M	Decay	$T_2 = 0.12 \text{ ms}; I_1 = 1/4; T_2 = 0.48 \text{ ms}; I_2 = 1/2; T_2 = 1.92 \text{ ms}; I_3 = 1/4;$ $M(t) = M_F(t) = 1/4 \exp(-t/0.12) + 1/2 \exp(-t/0.48) + 1/4 \exp(-t/1.92)$
N	Decay + 0.2% noise	$M(t) = M_M(t) + R^{0.002}$
O	Decay + 1% baseline	$M(t) = M_M(t) + 0.01$
P	Decay + flip angle artefacts	$M(t) = M_M(t) + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
Q	Decay + 0.2% noise + flip angle artefacts	$M(t) = M_M(t) + R^{0.002} + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
R	Decay + 1% baseline + flip angle artefacts	$M(t) = M_M(t) + 0.01 + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$
S	Decay + 0.2% noise + 1% baseline + flip angle artefacts	$M(t) = M_M(t) + R^{0.002} + 0.01 + 0.15 \cos(2\pi/0.2) \exp(-t/0.3)$

Appendix D: Determination of mass fractions by NMR

Notation

Cement notation is used throughout this Appendix. Hence, for instance, CH refers to calcium hydroxide and, in particular, H refers to water. AMU indicates atomic mass units and so that, for instance, CH^{AMU} is the mass of calcium hydroxide expressed in atomic mass units (approximately 74) while H_{CH}^{AMU} is the mass equivalent of water in calcium hydroxide, again expressed in atomic mass units (approximately 18, as CH is “made-up” of one molecule of water and one molecule of calcium oxide). The parameter β_x is introduced to mean inverse mass fraction of water in x . Hence $\beta_{CH} = CH^{AMU} / H_{CH}^{AMU} = 74/18$. Finally, m indicates actual mass measured in grams. So, for instance, m_{CH} is the mass of calcium hydroxide in a sample, while m_H^{pores} is the mass of water in pores. Signal fractions are designated I and mass fractions f .

Reference materials

The total mass of water contributing to the signal in a reference material is the sum of the water adsorbed into the pore spaces of the sintered α -alumina and the water equivalent in the calcium hydroxide:

$$m_H^{total} = m_H^{CH} + m_H^{pores} \quad (D.1)$$

It follows that:

$$m_H^{CH} = \frac{m_{CH}}{\beta_{CH}} \quad (D.2)$$

so that the fraction of chemically combined water equivalent based on the sample mass is:

$$f_{mass}^{sol-ref} = \frac{m_H^{CH}}{m_H^{CH} + m_H^{pores}} = \frac{m_{CH}}{m_{CH} + \beta_{CH} m_H^{pores}} \quad (D.3)$$

It is expected that this mass fraction equals the signal fraction attributed to the solids in the reference sample, I_{CH} .

A similar relationship holds for the water in each of the three pore types, viz.:

$$I_{pore}^{\alpha} = f_{mass}^{H\xi} = \frac{m_H^{\xi}}{m_H^{CH} + m_H^{pores}} = \frac{\beta_{CH} m_H^{\xi}}{m_{CH} + \beta_{CH} m_H^{pores}} \quad (D.4)$$

where $\xi = 1, 2, 3$ runs over the three pore sizes or T_2 components.

Cements

A similar argument can be developed for cements by which the signal fraction attributed to each relaxation component is equated with the water fraction in the associated component of the cement always provided that all the water in the sample is detected by the NMR experiment. If the methods advocated in this Guide are followed, then it can be expected that this condition will be met. Equations D.3 and D.4 hold for mass fractions of chemically combined water and water in each pore type in cements, respectively. If only instruments with a longer dead time are available, or if only CPMG experiments are carried out, then it is likely that signals attributable to solids will not be seen and this should be accounted for in the subsequent analysis. Dependent on the specifics of the cement examined, different components are to be identified.

What follows was first developed by Muller *et al.* ^[4] for a hydrated cement paste comprising (crystalline) solids: Portlandite (CH) and ettringite (ett); hydrates (C-S-H) with water divided between interlayer spaces (IL) and gel pores (gel); capillary pore water (cap) and anhydrous unreacted cement (uc). Empty voids (void) due to chemical shrinkage are also to be considered. Muller *et al.* write mass and volume conservation equations:

$$1 + (w/c) = (1 - \alpha) + (w/c) \left(\beta_{sol} I_{sol} + \beta_{C-S-H_{IL}} I_{C-S-H_{IL}} + \beta_{C-S-H_{gel}} I_{C-S-H_{gel}} + \beta_{cap} I_{cap} \right) \quad (D.5)$$

$$\text{and: } \frac{1}{\rho_{uc}} + \frac{w}{c \rho_H} = \frac{(1-\alpha)}{\rho_{uc}} + \frac{w}{c} \left(\frac{\beta_{sol} I_{sol}}{\rho_{sol}} + \frac{\beta_{C-S-H_{IL}} I_{C-S-H_{IL}}}{\rho_{C-S-H}} + \frac{\beta_{C-S-H_{gel}} I_{C-S-H_{gel}} + \beta_{cap} I_{cap} + \beta_{void} I_{void}}{\rho_H} \right) \quad (D.6)$$

Here, w/c is the water to cement mass fraction at mixing, and α is the degree of hydration. Finally ρ is density. For the solids:

$$\frac{w}{c} \beta_{sol} I_{sol} = \frac{w}{c} (\beta_{CH} I_{CH} + \beta_{ett} I_{ett}) \quad (D.7)$$

and:

$$\frac{w}{c} \frac{\beta_{sol} I_{sol}}{\rho_{sol}} = \frac{w}{c} \left(\frac{\beta_{CH} I_{CH}}{\rho_{CH}} + \frac{\beta_{ett} I_{ett}}{\rho_{ett}} \right) \quad (D.8)$$

Care needs to be taken in applying these results due to chemical shrinkage. If the sample is sealed cured, then the water at the time of measurement equals the water

at mixing and mass conservation holds. However, due to chemical shrinkage, the volume is not conserved. This is the origin of the term involving I_{void} in Equation D.6. I_{void} is the signal that would be seen if the shrinkage volume that is empty capillary porosity were filled with water. The size of this fictitious signal can be calculated by a separate (non-NMR) measurement of the shrinkage. Equally, it can be measured by NMR if the voids are subsequently filled with water, though filling them is difficult.

On the other hand, if the sample is cured underwater and the shrinkage volume that is capillary porosity pulls additional water into itself, then I_{void} is a real signal that takes the total signal fraction greater than 1 compared to the signal at the time of mixing, since:

$$I_{CH} + I_{ett} + I_{C-S-H_{IL}} + I_{C-S-H_{gel}} + I_{cap} = 1 \quad (D.9)$$

In many instances, of course, a sample meets neither of these conditions. It is perhaps not sealed immediately upon mixing, allowing a little of the mix water to evaporate. Alternatively it is not put underwater until it has started to set or it is a large sample. In either of these latter cases the diminishing permeability prevents the sample drawing water in uniformly throughout the sample volume. Data published by Chen *et al.* [46] suggests that this is true for samples as small as a few millimetres.

Numerical values for the more certain parameters include: $\rho_{uc, CH, ett, H} = 3.15, 2.24, 1.77$ and 1 g/cm^3 respectively; $\beta_{CH, ett} = 74/18$ and $1255/576$ respectively; and $\beta_{C-S-H_{gel}} = \beta_{cap} = 1$. The density and composition of the C-S-H inter-layer is variable. The density of water in small pores, especially interlayer spaces of hydrates is thought by some authors to be slightly greater than that of bulk water.

Muller *et al.* [4] show how, when coupled with knowledge of the chemical shrinkage and X-ray diffraction data for the Portlandite / ettringite mass balance and for the degree of hydration – the three unknowns in the equations – it is possible to determine the composition and density of the hydrates.

Equations D.5 to D.8 can be adapted to a range of scenarios for cements of different specification.

Appendix E: Reference Materials

Materials selection and manufacture

Reference materials are required to provide a multicomponent NMR T_2 relaxation time distribution that mimics the cement paste relaxation distribution. The materials are required to be both reproducible and stable. A study was carried out in 2015⁵ to identify candidate materials. Materials tested included: sintered α -alumina; sintered γ -alumina; zeolites ZSM-5 and 4A; sintered hydroxyapatite; calsilite; xonotlite; calcium hydroxide and polystyrene; variously doped with water and aqueous solutions of MnCl_2 , or sintered incorporating FeCl_3 , Fe_2O_3 and $\text{Fe}(\text{OH})_3$. The most promising materials were found to be based on sintered α -alumina doped with slightly acidic MnCl_2 solution to mimic the evaporable water fraction in different cement pore types, and powdered calcium hydroxide for the crystalline solids. None of the other trial materials showed completely useful responses, and results on them are not described here.

Sintered α -alumina pellets

The particle size of the α -alumina powder used in the study was very uniform and of the order of $0.2\ \mu\text{m}$. The powder was mixed with acetone and small grinding balls in a Turbula mixer in order to de-agglomerate the powder. After evaporation of the majority of the acetone, the powder mass was formed into cylindrical shapes using pellet press dies at a pressure of a few bars (pressed by hand only). The cylinders were sintered at $1000 - 1100\ ^\circ\text{C}$ to make pellets. SEM micrographs presented in Figure E.1 confirm that the distribution of sintered particle size is uniform, with submicrometre scale open porosity. In the dried state, the pellets do not give rise to any signal in hydrogen NMR experiments as expected. When the pellets are saturated with pure water, the water ^1H signal has a unimodal NMR distribution characterised by T_1 spin-lattice relaxation time of the order of $450 - 500\ \text{ms}$ and a T_2 spin-spin relaxation time of the order of $30 - 40\ \text{ms}$, as shown in Figure E.2a. The measurements were made at $20\ \text{MHz}$ using Spectrometer 12 from the Round Robin Trial. Both the material itself and the NMR distribution are reproducible. The relaxation time is expected to be dependent on the pore size of the α -alumina pellet which is in turn dependent on the original particle size. However, this has not been investigated.

⁵ Measurement standards for the NMR characterisations of cement based materials, University of Surrey and NPL, jointly funded by the UK EPSRC Impact Acceleration Account at University of Surrey and by NPL.

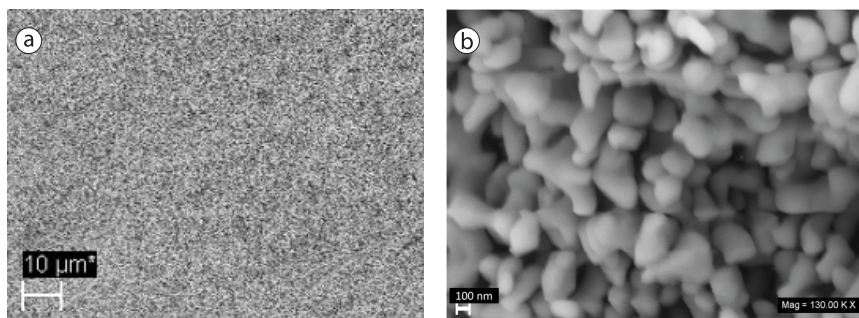


Figure E.1: SEM images of sintered α -alumina pellets confirming the homogeneity and pore size of sintered pellets. The scale bars are (a) 10 μm and (b) 0.1 μm .

The T_2 relaxation time of water within sintered α -alumina is much higher than the values observed for the evaporable (mobile) water within cementitious materials. The route to lowering the relaxation time is by addition of fast relaxing paramagnetic ions, as has been reported in literature^[57]. A solution of manganese chloride (MnCl_2) is commonly used. Known quantities of reagent grade MnCl_2 powder/beads were dissolved in distilled water to prepare solutions of different concentrations and the solutions used to saturate the pellets. The NMR T_2 distributions of samples filled with solutions of different MnCl_2 concentration are shown in Figure E.2b, alongside some examples from the bulk solutions. The dependence of both the T_1 and T_2 relaxation rates on the concentration of the MnCl_2 solution are characterised by a power law, as shown in Figure E.3a. The results show that by wetting with MnCl_2 solutions, the T_2 relaxation time can be controlled over a wide range that includes the required T_2 values identified as typical of cement-based materials. However, the requirement of long term stability of the NMR distribution is not fulfilled. The relaxation time slightly increases as time passes, on a timescale of weeks, Figure E.4.

To stabilise the solution chemistry and NMR distribution, the pH of the solution is made acidic. This is done by the addition of a small amount ($< 1\%$ by mass of solution) of nitric acid. The dependence of the T_2 relaxation rate on the concentrations of acidic MnCl_2 solution was evaluated and is shown in Figure E.3b. Through the wetting of α alumina cylinders with acidic MnCl_2 solution of controlled concentration, stable and reproducible mobile T_2 relaxation components can be produced (Figure E.4). The concentrations of acidic MnCl_2 solution used to achieve the cement characteristic T_2 relaxation times of about 100, 350 and 2000 μs are 250, 75 and 12 mM respectively *for the sub-micrometre alumina powder used in this study*. A modest pore size, and hence powder particle size, effect is expected, due to pore surface interactions.

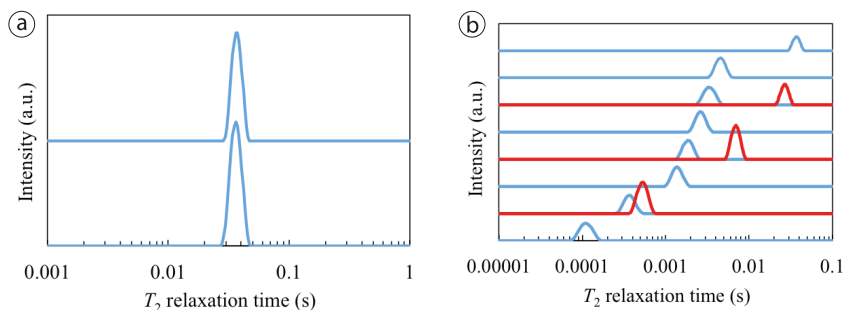


Figure E.2: (a) The T_2 relaxation time distribution of pure water in saturated α -alumina pellets sintered at: top, 1000; and bottom 1100 °C. The T_2 relaxation times are approximately 37 and 36 ms respectively. The distributions are drawn to the same scale, but vertically offset one from the next. (b) The T_2 relaxation time for solutions of $MnCl_2$ in saturated α -alumina pellets at concentrations of, from top, 0, 0.75, 1, 2, 4, 8, 50, 200 mM (blue lines). The corresponding T_2 distributions for bulk solutions at concentrations of 1, 4 and 50 mM are shown as red lines.

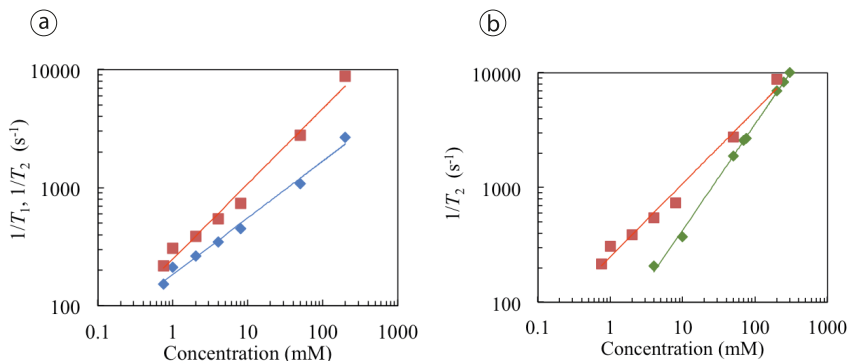


Figure E.3: (a) The T_2 (red line and points) and T_1 (blue) relaxation rates of $MnCl_2$ solution within sintered α -alumina pellets as a function of solution concentration. (b) The T_2 relaxation rate of $MnCl_2$ solution (red) and acidic $MnCl_2$ solution (green) within sintered α -alumina pellets.

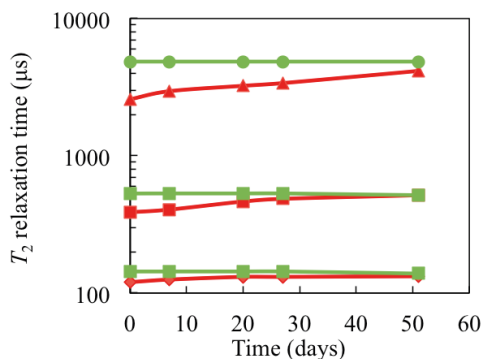


Figure E.4: The stability of the T_2 relaxation time of $MnCl_2$ solution at different concentrations in saturated pellets with (green) and without (red) the addition of nitric acid. From bottom, the pairs of lines and data point sets are for concentrations of 200, 50 and 4 mM respectively. The addition of nitric acid greatly improves the stability.

Calcium hydroxide

The contribution to the signal from crystalline solids in cements originates primarily from calcium hydroxide ($Ca(OH)_2$, Portlandite). Consequently, powdered calcium hydroxide can be used as a reference material. In the study, reagent grade calcium hydroxide was initially pressed into cylindrical pellets and dried at 120 °C for 48 hours, since as supplied calcium hydroxide seemingly adsorbs water as evidenced by NMR. Recorded solid echo signals of dried calcium hydroxide are presented in Figure E.5. The solid echo experiments of dried $Ca(OH)_2$ show no mobile signal. At the lower values of τ_q , the Gaussian - solid echoes are followed by a small negative signal. That is a well-known typical feature of a Pake doublet in the time domain^[31]. The Pake doublet is characteristic of dipolar coupled spin pairs in a (powdered) crystalline structure. There is no signal observed from the CPMG experiment. The lack of a mobile signal confirms that calcium hydroxide is a good material to represent the chemically combined water in a reference material.

A reference composite

The reference material study confirmed that it is not possible to mix pellets of doped solution saturated α -alumina and calcium hydroxide in a single sample and retain long term stability. Rather to achieve a cement mimic, at least four separate samples each sealed in a glass tube separated one from the next are required: three α -alumina and one calcium hydroxide. This does then raise issues of magnetic field homogeneity over the composite reference sample which is not itself homogeneous.

However, this is considered a small price to pay for what is otherwise a sample that can be readily used to test instrumentation and analysis procedures.

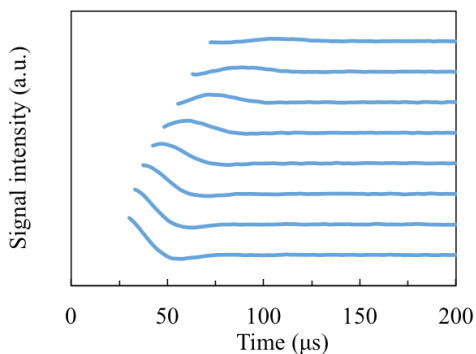


Figure E.5: Solid echo NMR signals recorded for reagent grade calcium hydroxide powder pressed into pellets. From bottom to top, the pulse gap τ_q is 12, 15, 19, 24, 30, 37, 45 and 54 μs . The curves, that asymptote to a zero baseline at long time, are shown to the same scale, vertically offset one from the next. The shape of the echo for a powder average of isolated spin 1/2 pairs of static nuclei can be calculated exactly. The shape is known as a Pake doublet, see text. It is reasonably approximated by a Gaussian centred on $2\tau_q$ modulated by a cosine also centred on $2\tau_q$ that creates the negative “wiggle”.

Appendix F: Round Robin Trial results

Materials and Methods

Materials and methods for the Round Robin Trial have been described previously in the main text, along with the results for a single paste mix. The result for that mix, and for the other five mixes examined in the Round Robin Trial are presented and compared in this appendix. The reproducibility of different instruments was considered in the chapter on the Round Robin analysis.

Independent analyses

The total water content of pastes prepared for measurement at different laboratories was determined independently using gravimetric analysis, knowing the initial sample mass and water to cement ratio, and the change in sample mass after hydration for 30 ± 2 days. The results are shown in Figure F.1. This was done because, during underwater hydration, additional water is drawn into the sample to fill the capillary voids created by chemical shrinkage. Hence the content of water within paste samples changes during hydration. Moreover, due to the diminishing permeability of the samples as they cure, the extent to which this happens, and the extent to which the capillary porosity is homogeneously water filled, are dependent on sample size (length and diameter) ^[46].

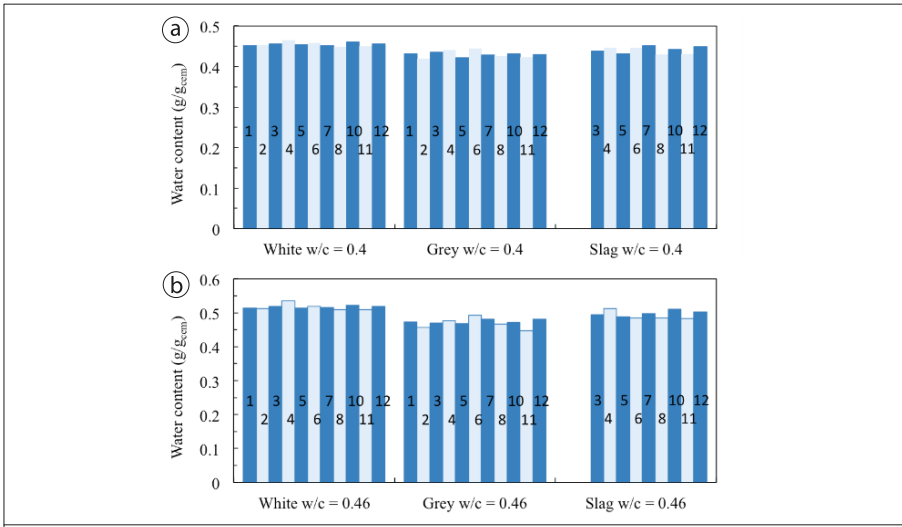


Figure F.1: The effective water to cement ratio for white, grey and slag cement pastes mixed at w/c ratio (a) 0.4 and (b) 0.46 by mass for measurement on different instruments: 1-12. Instrument 9 was not used due to the large probe size.

The content of water chemically bound into crystalline phases such as Portlandite and ettringite was measured independently by X-Ray diffraction (XRD) for a single paste of each mix. The results are presented in Table F.1. The results are used to calculate the fraction of water combined into the crystalline solids for direct comparison with the fractions determined from solid echo NMR results - see appendix D.

Table F.1:

Cement	g/g_{anhyd}				$g_{\text{H}_2\text{O}}/g_{\text{H}_2\text{O}}$			
	w/c	CH	Ett	$\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_{12}$	CH	Ett	$\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_{12}$	Sum
white	0.4	0.214	0.125	0.013	0.114	0.126	0.011	0.251
	0.46	0.224	0.133	0.012	0.105	0.118	0.009	0.232
grey	0.4	0.184	0.141	-	0.104	0.151	-	0.254
	0.46	0.198	0.140	-	0.102	0.135	-	0.237

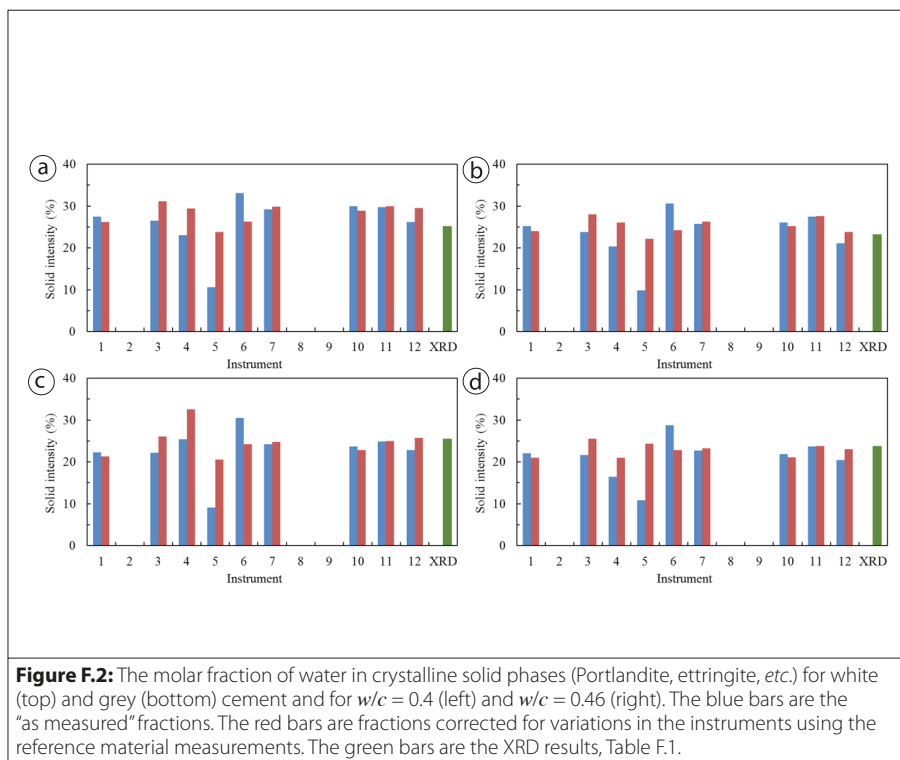
Table F.1: The mass fractions of Portlandite (CH), ettringite (Ett) and hemicarbo-aluminate ($\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_{12}$) in pastes (grams per gram anhydrous cement) measured by XRD and the calculated equivalent water mass fraction derived from those data.

NMR solid echo measurements

The fraction of chemically combined water within cement pastes was determined by back-extrapolation of the NMR solid intensity to nominally $\tau_q = 0$. Strictly the extrapolation was to zero pulse gap since τ_q is defined pulse centre to pulse centre, thus to $\tau_q = t_{p90\%}$ the pulse length. Measurements were made for the white, grey and slag cement. The results for white and grey cement are shown for each instrument by the blue bars in Figure F.2.

For the white and grey cements, the measured bound water fractions are spread quite widely between ~10 and ~30% with a standard deviation of the order of 5–6%. The wide spread of results arises partly because different instruments have different dead times and not all of them operate with sufficiently short τ_q . To take this into account, the results were normalised by the reference material calibration factor (section 7.4.2) measured for each instrument. These data are shown by the red bars in Figure F.2. The spread of results is substantially lower after this correction. For white cement paste with $w/c = 0.4$ and 0.46 it is $28.3 \pm 2.1\%$ and $25.2 \pm 1.7\%$ respectively. For grey cement paste it is $24.6 \pm 3.1\%$ and $22.8 \pm 1.4\%$ respectively. The mean content of chemically combined water for grey cement pastes agrees within 1% with

that established by the XRD measurement, as shown by the green bars in Figure F.2. The agreement for white cement pastes is less good, 2–3% difference. Nonetheless it remains within the experimental errors of both the XRD and NMR methods.



In the case of slag cements, the results are much less good. The main reason appears to be associated with the very short T_2^* of the pore water, and possibly with the less well-defined T_2 of water in interlayer spaces of C-A-S-H. This makes it much more difficult to separate the solid echo from the mobile water signal. An example of the associated data fitting that illustrates this problem is shown in Figure F.3. Hence, no quantitative conclusions on the crystalline component of the slag cements were made.

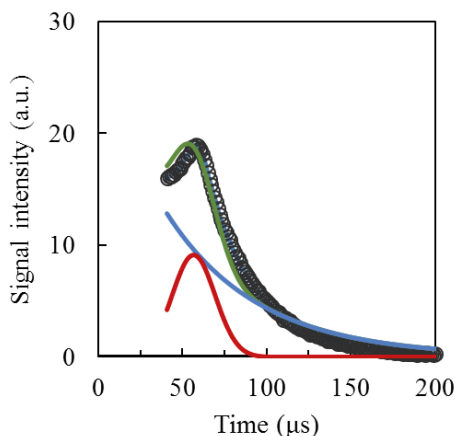


Figure F.3: Slag solids demonstrating fit quality. The green line is the fit to the data composed of the exponential (blue) and gaussian (red) fits.

NMR CPMG measurements

The mobile water fraction was characterised using CPMG for each of the three cement paste types: white, grey and slag; at each of the water to cement ratios, 0.4 and 0.46. Results were analysed using both inverse Laplace transform and constrained multi-exponential fitting.

There is a range of instrumentation and experimental parameters that have an important influence on the measured T_2 relaxation time distribution when performing CPMG experiments. These can have both a positive and negative influence on the experimental outcome. Table F.2 presents the NMR parameters that materially affect the experiments performed using each spectrometer within the Round Robin Trial.

A key parameter affecting the accuracy of the inverse Laplace transform of CPMG data is the signal to noise ratio. Figure F.4 presents the signal to noise ratio for CPMG measurements of cement pastes measured with different instruments. The signal to noise varies by more than a factor of 10 for essentially the same experiments. It is noted that signal to noise ratio is generally low using instruments 5 and 6. Also, oscillatory artefacts in the first few echo intensities due to poorly set pulse flip angles or poor B_1 homogeneity can have a detrimental effect on the results. However, these are not always obvious in the steeply decaying intensities of these first few echoes. An example was shown in Figure 13 in the main text.

The analysis of CPMG decays by inverse Laplace transform was performed as described in the main text. In the trial, the algorithm due to Venkataramanan *et al.* ^[51] was used. This algorithm makes the assumption that the distribution function is non-negative and introduces a regularisation (“smoothing”) parameter that was chosen for each instrument based upon the analysis of the reference materials.

White cement paste, $w/c = 0.4$. The NMR T_2 distribution of white cement paste mixed at $w/c = 0.4$ is presented in Figure F.5. At first sight, these distributions all look very different one to the next. The differences can be explained by variations in the instrumentation and samples as discussed in the following paragraphs. At the end, it is found that a favourable comparison can be made between five like-for-like systems.

It is seen that about one quarter of the data contain an inverse Laplace transform artefact at the lowest T_2 values (below $\approx 30 \mu\text{s}$). This is below the minimum echo time and so represents an attempt to fit data where no data exist. Hence any peaks of the distribution with a maximum amplitude appearing below $30 \mu\text{s}$ are discarded. In Figure F.5 they are shaded blue.

Table F.2:

Instrument	Advantages	Disadvantages
1	Short P_{90} Very good SNR	
2	Good SNR for white cement	First $\tau = 64 \mu\text{s}$ long Low SNR for grey cement
3	Short dead time Short P_{90} and P_{180} Very good SNR for white and slag ($w/c = 0.46$) cement Good SNR for grey and slag ($w/c = 0.4$) cement	
4	Short P_{90} Good SNR	Long dead time
5		Variable SNR Long dead time
6	Short P_{90} and P_{180}	Very low SNR First $\tau = 26 \mu\text{s}$ too short due to software misunderstanding
7	Very good SNR Short dead time ($10 \mu\text{s}$)	Short total CPMG decay ($t_{\text{max}} = 0.33 \text{ s}$) leading to poorly defined baseline due to software limitation as programmed
8	Good SNR	First $\tau_1 = 88 \mu\text{s}$ long Long dead time
10	Short dead time Short P_{90} and P_{180} Good SNR for white and slag cement	Low SNR for grey cement
11	Very good SNR	First $\tau = 64 \mu\text{s}$ long
12	Very good SNR Short P_{180}	

Table F.2: Summary of advantages and disadvantages of the different instruments for CPMG analysis of cements. In the table, short and long are defined as: short $P_{90} < 4 \mu\text{s}$; short $P_{180} < 6 \mu\text{s}$; short dead time $< 10 \mu\text{s}$. Moreover, very good signal to noise ratio is defined as $\text{SNR} > 1000$; good $\text{SNR} > 500$; low $\text{SNR} < 500$; very low $\text{SNR} < 300$.

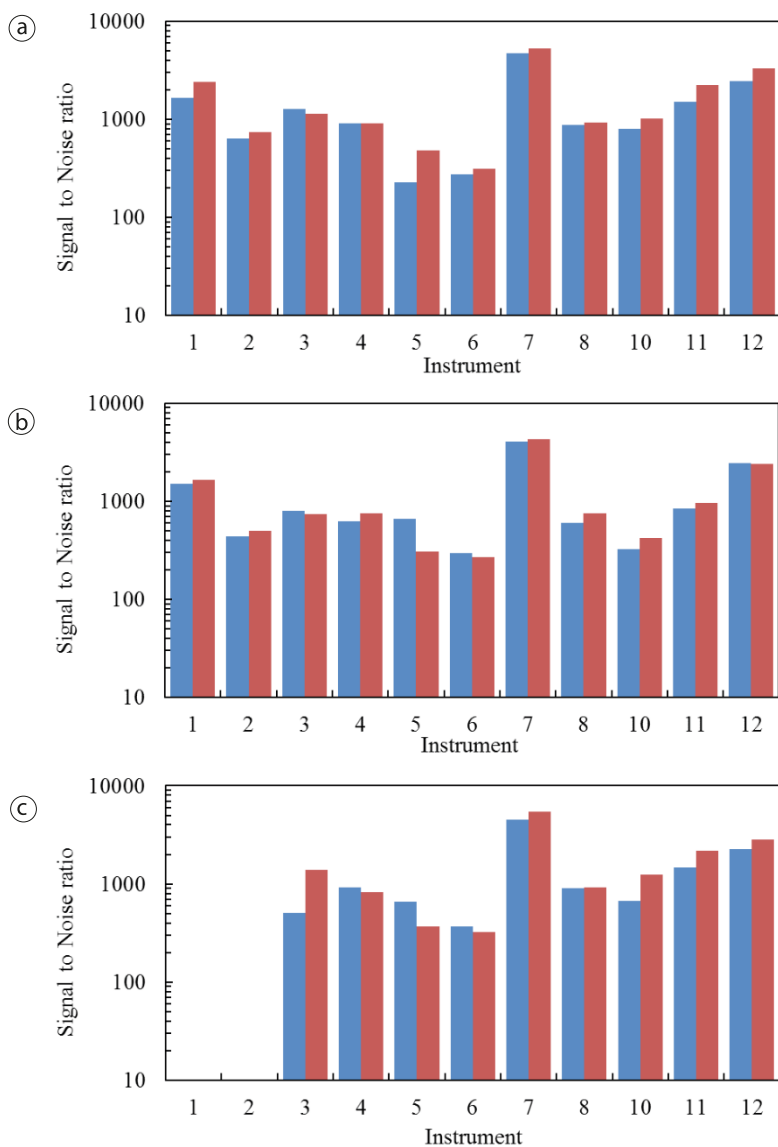


Figure F.4: Signal to noise ratio of the CPMG data for different instruments. (a): white cement; (b): grey cement; and (c): slag cement. Blue bars are for mixes with $w/c = 0.4$; red with $w/c = 0.46$.

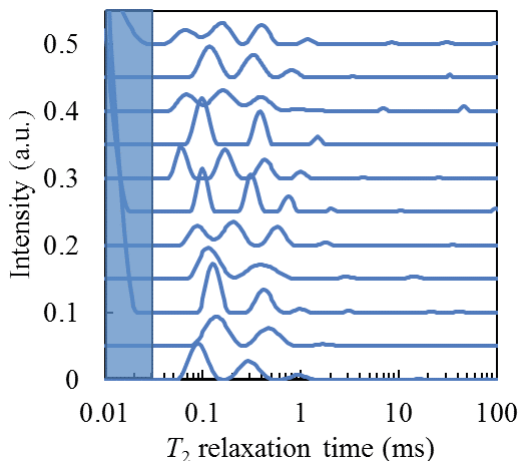


Figure F.5: T_2 distribution map of white cement paste with $w/c = 0.4$ determined by inverse Laplace transformation. From bottom, the traces are for instruments 1...12 excluding 9. They are drawn to the same scale, each offset 0.05 units from the next.

The intensities of individual mobile components are calculated based on the area of peaks – the integrated peak intensity. This is because it is known that the peak amplitude and widths depend strongly on the inverse Laplace transform regularisation parameter but that the areas show much weaker dependence. The intensities are presented in Figure F.6a (as a percentage of total mobile water) for the three main peaks typically appearing in the range 0.1 to 1 ms as well as the sum of all the remaining higher T_2 peaks. The actual ^1H fractions in each reservoir in the paste are, of course, this fraction of the mobile ^1H resultant from the solid echo measurement. The T_2 of the maximum of the three main peaks is presented in Figure F.6b.

At first sight there is considerable variation across the data sets. However, much of this is explicable when the experimental circumstances and the cement used are considered.

The first observation is that in several instances, the peak at around 0.1 ms that has been associated with inter-layer water in C-S-H hydrates in published results of white cement emanating from the Nanocem consortium, *e.g.* ^[4], is split into two. This phenomenon has been seen beyond this Round Robin Trial. The white cement used here has a significantly higher C_3A fraction than that used in the study by Muller *et al.* It is speculated that this is the primary cause of the effect - the C_3A cement has more ettringite and C-A-S-H.

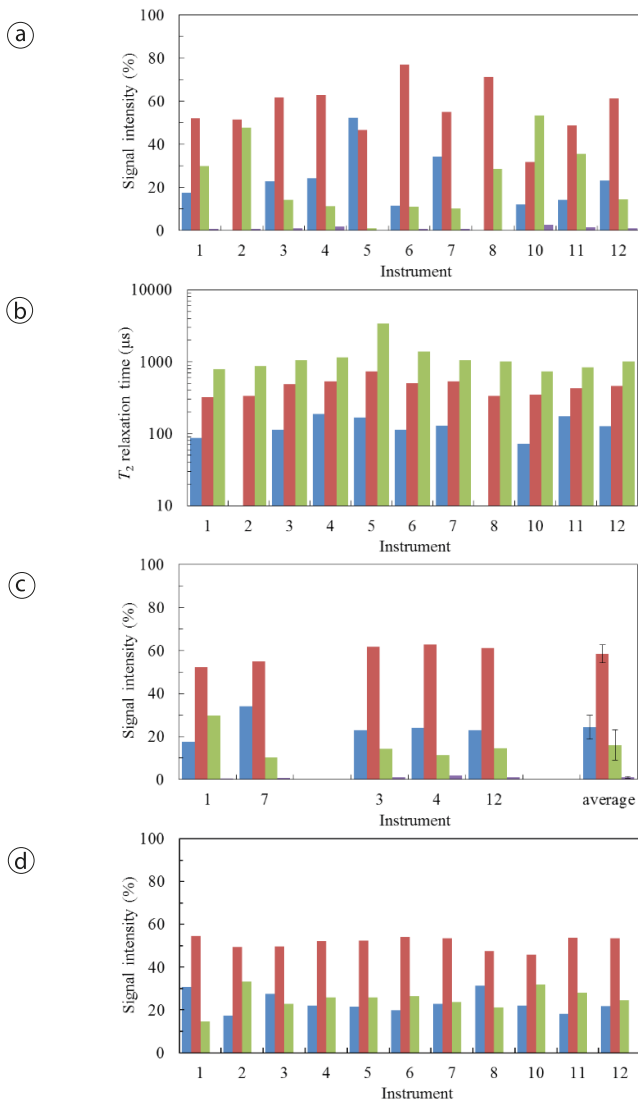


Figure F.6: a) The mobile T_2 component intensity distribution for white cement paste with $w/c = 0.40$ determined by inverse Laplace transformation for the three main peaks (blue, red, green) and the sum of all the remaining peaks presented as 4th component (purple). b) The T_2 values of the maximum of the three main peaks. c) Intensity results for the comparable 10 mm probes of instruments 3, 4 and 12 and the 18 mm probes of instruments 1 and 7 together with their average. d) The intensity distribution determined by constrained 3 component exponential fitting.

For the subsequent analysis here, where this split occurs, the two peaks are combined and assigned an average relaxation time.

The second observation is that the measurements have been carried out using samples of different size for probe diameters ranging from 10 mm to 38 mm, almost a factor of 4 difference. The degree of hydration depends critically on the availability of water. Smaller samples are more able to draw in water during underwater curing than larger samples. Also, it is known that larger samples undergo less macroscopic shrinkage than smaller samples so that the amount of filled capillary porosity is different ^[46]. Consequently, the experiments do not always compare like with like. The 10 mm probes that can be compared directly are those for instruments: 3; 4; 6; 10; and 12. There are three ~18 mm probes: instruments 1; 7; and 8. Finally, there are two about 25 mm: instruments 5 and 11.

The third observation is that the measurements using instruments 2, 8 and 11 have been performed with the first τ value more than twice that proposed in this Guide: 64, 88 and 64 μ s respectively. With such a long first echo time, the first component of the NMR cement mobile T_2 distribution is at best poorly differentiated from the next, at worst not resolved at all. Hence these data should likely be treated with caution.

The fourth observation is that the data from instruments 5 and 6 have a substantially lower signal to noise ratio than is advisable for the inverse Laplace transform. Hence, for Laplace inversion analysis these results also should be treated with caution.

Finally, we note that instruments 10 and 11 have a sample space temperature of 40 °C, significantly higher than all the rest for measurements of cement paste. This causes evaporation and redistribution of water within the sample and potentially varies the T_2 times. Heating of the sample in these instruments was evidenced by regular breaking of the glass tubes due to increased pressure, probably resulting in water loss from the samples by evaporation.

If like-for-like are to be compared, this really leaves the 10 mm probe data of instruments 3, 4 and 12 or the 18 mm probes of instruments 1 and 7. All these data are acquired at about 20 MHz. Inspection of Figure F.6c shows excellent agreement between the 10 mm measurements, and quite good agreement when the two 18 mm experiments are added in. For these five, the mean and standard deviation of the three main peak intensities are: $24.4 \pm 5.4\%$; $58.6 \pm 4.2\%$; and $16.1 \pm 7.1\%$. These averages are presented as the final set of bars in Figure F.6c. If the comparison is restricted to just the 10 mm probes, then it is: $23.4 \pm 0.5\%$; $61.9 \pm 0.6\%$; and $13.4 \pm 1.5\%$ suggesting that the larger sample size has significant impact, perhaps due to inhomogeneous curing.

The ILT data fitting is compared to a three-component constrained multi-exponential fit, as shown in Figure F.6d. For general application, where signal to noise may be an

issue and where there is some prior knowledge of the sample, constrained multi-exponential fitting could be a preferred analysis route. The fits were made based on three components with floating amplitudes and relaxation times constrained to: 129 μs , 467 μs and 1010 μs . These relaxation times are the average of those discovered by ILT for the five experiments identified in the previous paragraph. The values are extremely close to those used in other analyses of this sort. The coefficient of determination (R^2) for individual fits is very good: above 0.99. It is seen that the five experiments identified above continue to be in good agreement. The biggest outlier is instrument 1. However, several of the other experiments that were discounted for want of good signal to noise ratio, or for want of a short first echo time, are seen to come into line as well. A good example of the former is instrument 6 which has a short echo time and 10 mm probe, but low signal to noise. The agreement with instruments 3, 4 and 12 is now good. It is also in reasonable accord even with instrument 10, also a 10 mm probe where the temperature is higher, suggesting that forcing the T_2 values enables one accurately to pull out the component intensities. The average intensities of the three components across all eleven instruments are: $23.2 \pm 4.5\%$, $51.5 \pm 2.8\%$ and $25.3 \pm 4.9\%$.

White cement paste $w/c = 0.46$. The NMR T_2 distribution of white cement paste mixed at $w/c = 0.46$ is presented in Figures F.7 and F.8. Identical considerations as discussed in the previous section suggest that only the 10 mm probes for instruments 3, 4 and 12 or the 18 mm probe data for instruments 1 and 7 should be retained. The component intensities for these five are shown in Figure F.8c. Once more, broad agreement is seen. We note that in both the $w/c = 0.4$ and 0.46 samples, instrument 7 (18 mm probe) data shows systematically more first peak intensity than instrument 1 (also 18 mm) and indeed the other instruments more generally. This may be the result of an oscillatory artefact in the first few echoes, and hence an artefact associated with the inverse Laplace transform for this instrument.

The three-component multi-exponential fitting with constrained T_2 relaxation times was also performed for white cement $w/c = 0.46$ samples. The results are presented in Figure F.8d. As before, the three mobile relaxation times were constrained to the average of the T_2 values obtained by ILT analysis for instruments 1, 3, 4, 7 and 12. They are: 133, 495, and 1183 μs . The coefficient of determination (R^2) for individual fits is very good: above 0.99. In general the reasonable agreement between data across all 11 instruments was found with the average ($\pm$ standard deviation) intensities of the components 20.5 ± 4.5 , 44.0 ± 4.9 and $35.5 \pm 5.2\%$ respectively.

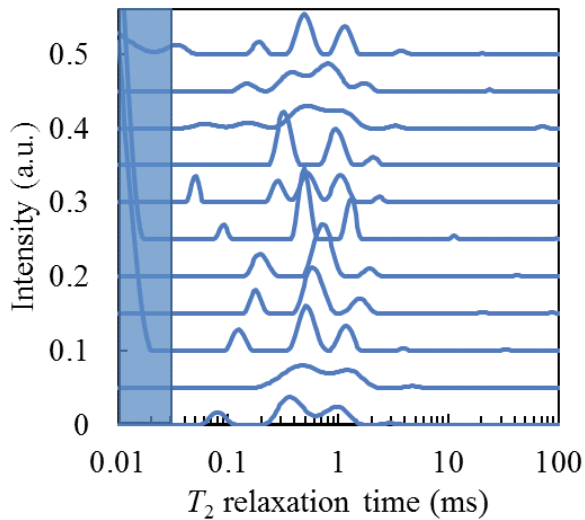


Figure F.7: T_2 distribution map of white cement paste with $w/c = 0.46$ determined by inverse Laplace transformation. From bottom, the traces are for instruments 1...12 excluding 9. They are drawn to the same scale, each offset 0.05 units from the next.

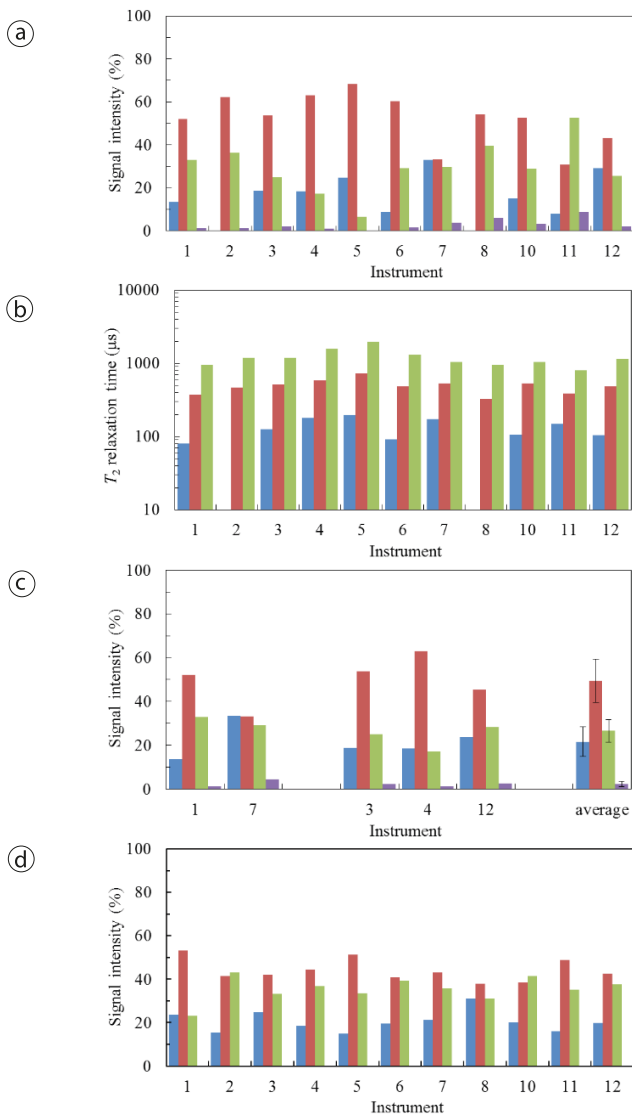


Figure F.8: a) The mobile T_2 component intensity distribution for white cement paste with $w/c = 0.46$ determined by inverse Laplace transformation for the three main peaks (blue, red, green) and the sum of all the remaining peaks presented as the fourth component (purple). b) The T_2 values of the maximum of the three main peaks. c) Intensity results for the comparable 10 mm probes of instruments 3, 4 and 12 and the 18 mm probes of instruments 1 and 7 together with their average. d) The intensity distribution determined by constrained three-component exponential fitting.

Grey cement paste $w/c = 0.4$. The NMR T_2 distribution of grey Portland cement paste mixed at $w/c = 0.4$ is presented in Figure F.9 for all the participants. The intensity, as a percentage of total mobile water, and T_2 results determined from inverse Laplace transformation are presented in Figures F.10a and b respectively. As with white cement, where the peak at $T_2 \approx 0.1$ ms peak is split, the two fractions are combined. The same considerations as before apply. In particular, the data for instrument 6 have an unusually low signal to noise ratio, as do, in this particular case, instrument 10 data (which also has higher temperature). Again instruments 2, 8 and 11 have a long first echo time. Notwithstanding these differences, there is actually quite reasonable agreement across many of the experiments. However, for consistency, we select just those five that can be compared as before. The intensities of these are replotted alone in Figure F.10c to aid visual comparison. For the five similar instruments, the first peak intensity has a mean and standard deviation of $62.7 \pm 4.3\%$; the second peak $30.4 \pm 5.0\%$; and the third $4.5 \pm 1.4\%$. It is noticeable how the relative intensity of the first and second peaks (hydrate interlayer and gel pore water respectively) are reversed in grey cement paste compared with white.

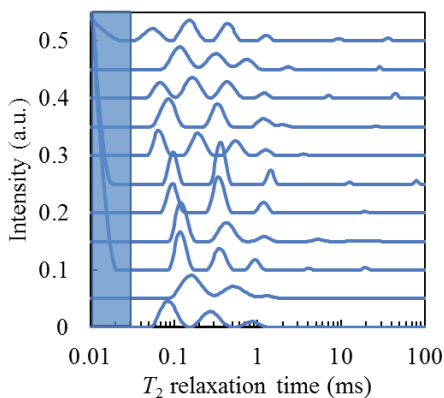


Figure F.9: T_2 distribution map of grey cement paste with $w/c = 0.4$ determined by inverse Laplace transformation. From bottom, the traces are for instruments 1...12 excluding 9. They are drawn to the same scale, each offset 0.05 units from the next.

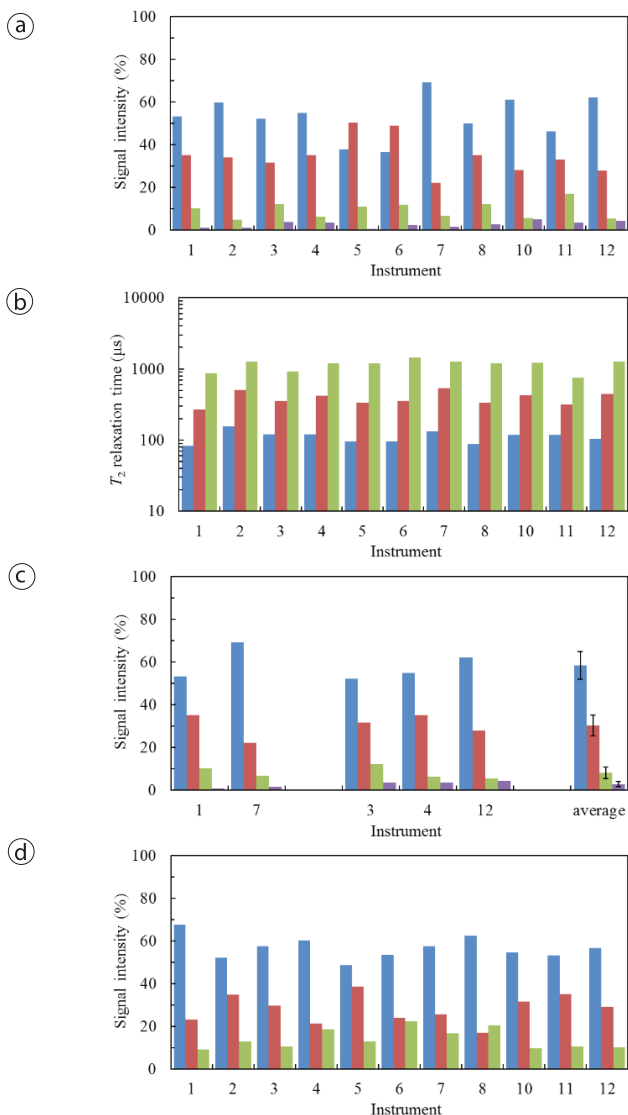


Figure F.10: a) The mobile T_2 component intensity distribution for grey cement paste with $w/c = 0.4$ determined by inverse Laplace transformation for the three main peaks (blue, red, green) and the sum of all the remaining peaks presented as the fourth component (purple). b) The T_2 values of the maximum of the three main peaks. c) Intensity results for the comparable 10 mm probes of instruments 3, 4 and 12 and the 18 mm probes of instruments 1 and 7 together with their average. d) The intensity distribution determined by constrained 3 component exponential fitting.

Constrained multi-exponential fitting of grey cement paste data was performed with T_2 relaxation times set to 110, 387 and 1411 μs (average values of T_2 of the five selected data sets shown in Figure F.10c). The T_2 values for first two components are $\approx 15 - 20\%$ shorter than for white cement paste as expected due to higher paramagnetic impurity content. The coefficient of determination (R^2) for the majority of the fits is very good: above 0.99. In the case of fits for data measured using instruments 4, 10 and 12 (all 10 mm probes) the coefficient of determination is somewhat lower than elsewhere as there is an additional long component present in the decay. For these data sets, the fittings were performed additionally including a fourth component at 40 ms. A very good reproducibility of results is found, Figure F.10d. The discrepancies of results across all participants of Round Robin Trial are 4–5% for first and second components and $\sim 2\%$ for third component. The average values of intensities based on exponential fitting are 59.2, 32.7 and 7.2%, in good agreement with the ILT based calculation.

Grey cement paste, $w/c = 0.46$. Figures F.11 and F.12 repeat Figures F.9 and F.10 for the grey cement samples prepared at $w/c = 0.46$. The data obtained using instruments 5 and 6 are outliers but also have very low signal to noise ratio. The other outlier is instrument 11. This could be affected by the combined higher measurement temperature and longer first τ . Despite these three data sets, fair agreement between the NMR signal intensities is observed (Figure F.12a), with average intensities of components: $57.9 \pm 5.9\%$; $31.2 \pm 4.4\%$; and $8.0 \pm 2.9\%$ for all remaining measurements. For like-with-like measurements using 10 mm probes on instruments 3, 4 and 12 and 18 mm probes on instruments 1 and 7 (Figure F.12c) the average intensities are very similar: $58.4 \pm 6.4\%$, $30.5 \pm 4.9\%$ and $8.3 \pm 2.6\%$.

Slag cement paste $w/c = 0.4$. The NMR T_2 distribution of slag cement paste mixed at $w/c = 0.4$ is presented in Figure F.13. The intensity expressed as a percentage of total mobile water and T_2 results are presented in Figure F.14a–d. Additional to instrument 9, slag cement paste was not measured using instruments 1 and 2.

The biggest issue with the slag cement results is assigning the peaks. In one case, instrument 6, there is a peak at around 100 μs that may be due to hydrating (alumina?) phases in the (amorphous) slag that is picked up by the low first echo time. The first peak with instrument 12 has a low T_2 as it may be tending to pick up this component too. On the other hand, the data for other instruments appears to be missing a peak. It is as if the interlayer and part of the gel peak gives rise to a single peak somewhere in the middle and similarly the other part of the gel and interhydrate peaks are averaged. This may be due to pearling of the Laplace inversion. If this is the case, for instance with instruments 3 and 11, then in the data tables and graphs, the gel peak is mis-assigned to the interlayer and so forth. There is a large variation in the intensity of third peak ranging from $\approx 2\%$ to 20%. There seems

to be a correlation between the intensity of this peak and the inverse relaxation time, perhaps also an artefact of the inverse Laplace transformation. When all this is considered one is left with reasonable agreement between instruments 4, 5, 7, 8 (notwithstanding a long first echo time), and to a lesser extent 12.

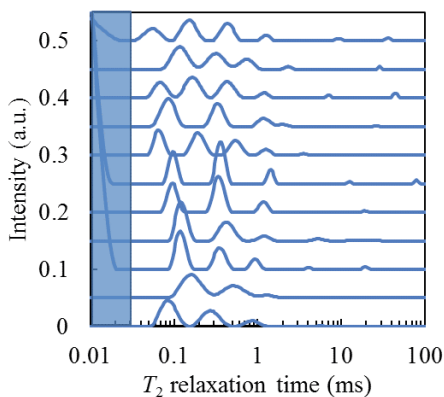


Figure F.11: T_2 distribution map of grey cement paste with $w/c = 0.46$ determined by inverse Laplace transformation. From bottom, the traces are for instruments 1...12 excluding 9. They are drawn to the same scale, each offset 0.05 units from the next.

Following the analysis of white and grey cement pastes, three-component constrained multi-exponential fitting has also been performed for slag cement paste using constrained T_2 values. The results of that fitting are shown in Figure F.14d. The T_2 values used (207, 740 and 2214 μs) are the average inverse Laplace transform T_2 values for instruments 4, 5 and 12 (10 mm probes) and 7 (18 mm probe). Reasonably good agreement is observed. The two first components contribute almost equally towards intensity, giving on average of: $43.5 \pm 4.8\%$ and $40.3 \pm 4.5\%$ respectively. The third component has average intensity of $16.2 \pm 2.1\%$ across all 9 instruments used.

Slag cement paste $w/c = 0.46$. The NMR T_2 distribution of slag cement paste mixed at $w/c = 0.46$ is shown in Figure F.15. The intensity and T_2 results are presented in Figure F.16a-d. Very similar observations can be made about slag cement at $w/c = 0.46$ as at $w/c = 0.4$. Multi-exponential fitting (Figure F.16d) was performed with T_2 constrained to 175, 608 and 1778 μs . The variability between instrument intensities are bigger than for slag cement with $w/c = 0.4$: $36.3 \pm 7.7\%$; $38.9 \pm 7.9\%$; and $24.8 \pm 4.0\%$. The main difference is in higher average intensity of third component, as expected with a higher w/c ratio.

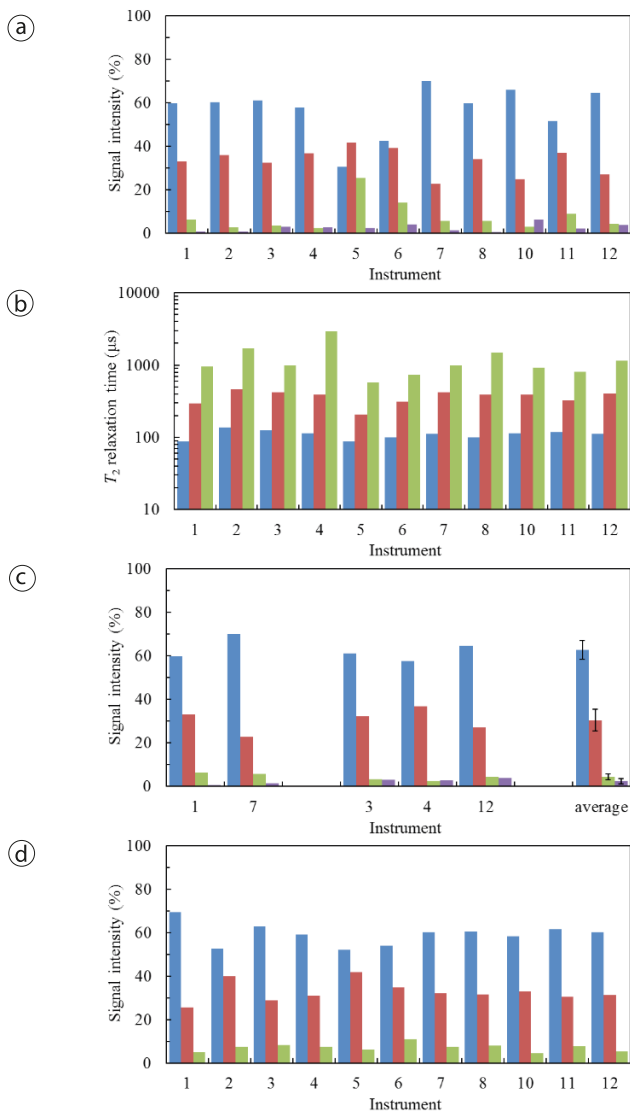


Figure F.12: a) The mobile T_2 component intensity distribution for grey cement paste with $w/c = 0.46$ determined by inverse Laplace transformation for the three main peaks (blue, red, green) and the sum of all the remaining peaks presented as the fourth component (purple). b) The T_2 values of the maximum of the three main peaks. c) Intensity results for the comparable 10 mm probes of instruments 3, 4 and 12 and the 18 mm probes of instruments 1 and 7 together with their average. d) The intensity distribution determined by constrained three-component exponential fitting.

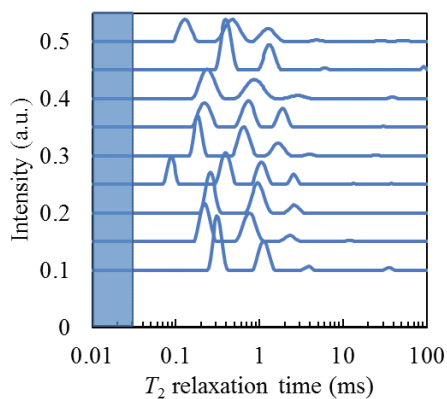


Figure F.13: T_2 distribution map of slag cement paste with $w/c = 0.4$ determined by inverse Laplace transformation. From bottom, the traces are for instruments 3...12 excluding 9. They are drawn to the same scale, each offset 0.05 units from the next.

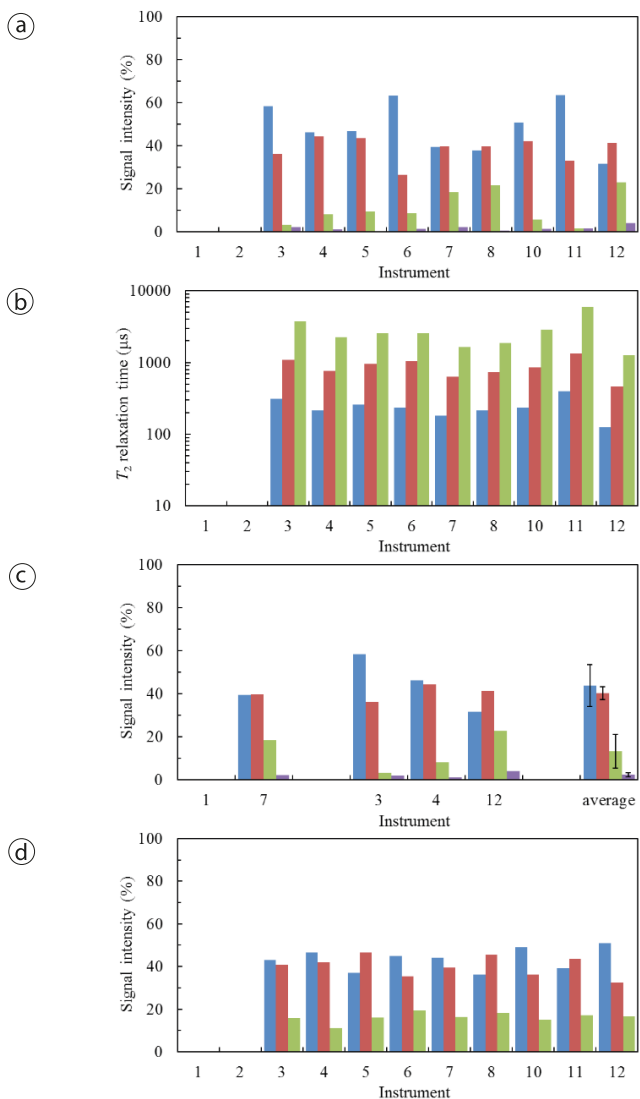


Figure F.14: a) The mobile T_2 component intensity distribution for slag cement paste with $w/c = 0.4$ determined by inverse Laplace transformation for the three main peaks (blue, red, green) and the sum of all the remaining peaks presented as the fourth component (purple). b) The T_2 values of the maximum of the three main peaks. c) Intensity results for the comparable 10 mm probes of instruments 3, 4 and 12 and the 18 mm probe of instruments 7 together with their average. d) The intensity distribution determined by constrained three-component exponential fitting.

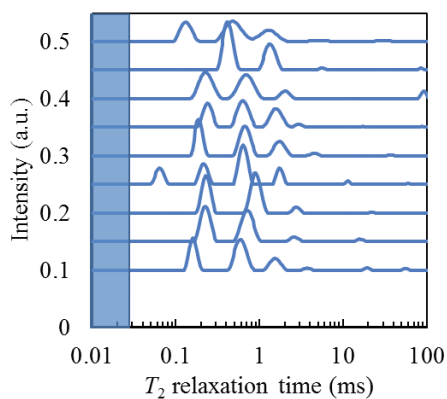


Figure F.15: T_2 distribution map of slag cement paste with $w/c = 0.46$ determined by inverse Laplace transformation. From bottom, the traces are for instruments 3...12 excluding 9. They are drawn to the same scale, each offset 0.05 units from the next.

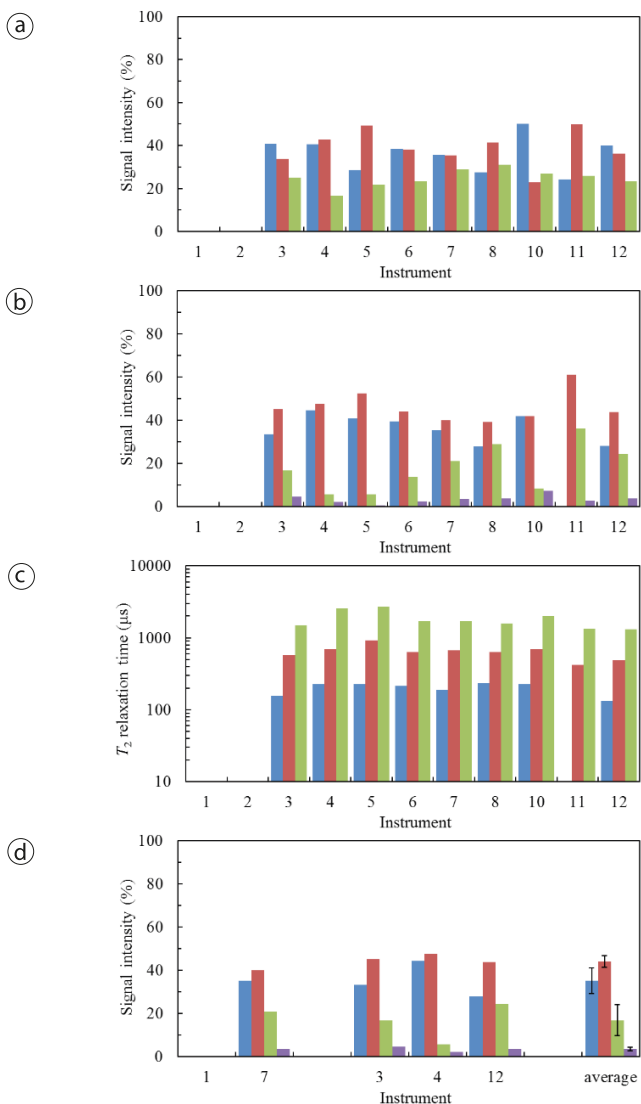


Figure F.16: a) The mobile T_2 component intensity distribution for slag cement paste with $w/c = 0.46$ determined by inverse Laplace transformation for the three main peaks (blue, red, green) and the sum of all the remaining peaks presented as the fourth component (purple). b) The T_2 values of the maximum of the three main peaks. c) Intensity results for the comparable 10 mm probes of instruments 3, 4 and 12 and the 18 mm probe of instrument 7 together with their average. d) The intensity distribution determined by constrained three-component exponential fitting.

The Characterisation of Cement Based Materials Using T_2 ^1H Nuclear Magnetic Resonance Relaxation Analysis

Good Practice Guide No. 144

What is it about?

This Guide is an introduction to the basic concepts of using ^1H nuclear magnetic resonance (NMR) relaxometry to determine the state of water in cement, and hence the degree of cure of the cement and the cement microstructure, in particular the porosity. The Guide provides information on calibrating the equipment, the NMR responses that can typically be found from cement and how to quantify the information obtained. Recommendations are made for the specification of suitable equipment, the set-up procedures required, and the experiments to be performed. Detailed results of an international Round Robin Trial are included to demonstrate the usability, repeatability and accuracy of the method. The preparation of suitable non-cementitious reference materials is also discussed.

Who is it for?

This Guide is intended for materials scientists and technologists in the cement and cement additive production industry, as well as those involved in the characterisation of cements of existing structures and during new build. It is also of value to non-NMR specialists seeking to use NMR as a cement characterisation tool in academia, standards laboratories, buildings test facilities, and similar organisations. The Guide will also assist those seeking to design and manufacture NMR equipment targeted at the cement industry. Finally, those looking to introduce NMR for the study of alternate porous media will find highlighted many of the general pitfalls associated with the technique.

What is its purpose?

This Guide is intended to promote the concept of NMR as both a research and a quality assurance tool, and to encourage the design and manufacture of suitable equipment for both laboratory and field use.

What is the prerequisite knowledge?

This Guide assumes a moderate level of physics background, as well as some understanding of cement chemistry.

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