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P-01

MATRIX FACTORISATIONS FOR THE ESTIMATION OF NMR RELAXATION DISTRIBUTIONS

Paul Teal

Victoria University of Wellington, Wellington, New Zealand

The interpretation of nuclear magnetic resonance (NMR) measurements involves the estimation of the distribution of relaxation times. This is typically performed using the numerically ill-conditioned inversion of a Laplace transform.

The most successful methods of performing this inversion for multi-dimensional distributions are the approaches of Venkataramanan et al (2002), and Chouzenoux et al (2013). The former uses a data compression stage followed by application of the Butler-Reeds-Dawson (BRD) algorithm. The latter directly applies classical interior point methods, with matrix inversion performed using a preconditioned conjugate gradient (PCG).

The fact that both of these methods are presented using truncated singular value decomposition (TSVD) of matrices representing the exponential kernel gives the two methods a superficial resemblance. This is because the SVD is such a general matrix decomposition. There are however other matrix factorisations that are applicable to each of these algorithms, and which demonstrate the different fundamental principles behind the operation of the algorithms.

In the case of the data compression approach, the goal is to obtain a matrix factorisation which separates orthogonal components of the kernel matrices which are non-zero from those which are (with a given machine precision) indistinguishable from zero. Although the SVD will do this, the matrix decomposition specifically designed for this task is the rank-revealing QR (RRQR) factorisation (Gu et al, 1996).

In the case of the interior point method, the matrix decomposition is used to construct an efficient preconditioner. The important matrices are not the kernel matrices, but their products with their respective transposes, which are square matrices. An effective choice of factorisation in this case is the LDL with diagonal pivoting, also known as the Bunch-Kaufman-Parlett factorisation. (Bunch et al, 1977).

The inversion process in each cases is shown to be numerically identical with that obtained using the SVD.

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P-02

NMR RESPONSE INTEGRATING METHOD FOR MULTI-SUBSAMPLES OF POROUS MEDIA BASED ON DIGITAL CORE

Yulong Zou¹, Ranhong Xie¹, Kang Liu¹, Falong Hu², Chaoliu Li²

¹State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China,

²Research Institute of Petroleum Exploration & Development, PetroChina, Beijing, China

Numerical simulation of pore-scale NMR response is becoming a research focus, which contributes to better understanding the NMR relaxation mechanism in porous media. In the tight or serious heterogeneous reservoirs, however, the simulated NMR responses of porous media from micro-CT often mismatch the actual measurements of the core samples. The main reasons are a low-resolution CT scan is insufficient to identify the micropores of entire core sample; while a high-resolution CT scan of a small sample does not reflect the pore structure of the entire core sample. This paper proposed a NMR response integrating method of porous media that used multi-subsampling in high-resolution CT scan. An equation for NMR response integrating was provided. The validation used two types of digital core models. The first type was the sedimentary digital core model from physical-based reconstructing method, which simulated the sedimentation, compaction and cementation processes of sedimentary rock. The second type was the tight sand digital core model from CT scans. The integrating method first simulated the NMR response of entire porous media by random-walk algorithm, and divided the entire porous media to 8 subsamples from 2x2x2 decomposition. The NMR response of each subsample was simulated respectively. The NMR responses of all subsamples were finally integrated to obtain the integrated NMR response, which was compared with the response of entire porous media. The results showed that the integrated NMR response could better reflect the NMR characteristic of entire porous media than any single subsample.

Acknowledgements:

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P-03

AN IMPROVED TSVD ALGORITHM FOR NMR T_2 DISTRIBUTION IN SHALE RESERVOIRS AND ANALYZING INFLUENCE FACTORS

GAO Yang, XIAO Lizhi

China University of Petroleum-Beijing, Beijing, China

In shale reservoirs, due to the low porosity and very low permeability, the SNR (signal to noise ratio) is very low, usually in NMR logging the SNR is less than 5. And due to the nanometer pore size, the surface relaxation is very strong hence, the echo trains decays very fast. Though truncated singular value decomposition (TSVD) algorithm is widely used for conventional NMR transverse relaxation (T_2) inversion, the high SNR requirement restricts this algorithm to the shale reservoirs. In this article, we find a new method to determine the truncated singular value, and we use simultaneous iterative reconstruction technique (SIRT) algorithm to non-negative

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restriction. The new algorithm not only suit to conventional reservoirs, but also to shale reservoirs. Digital simulations show that the inversions inversed by this algorithm are consistent to the model when SNR=10. Core analysis logging inversions also show that this algorithm works very well for low SNR. In this new algorithm, we just decompose the singular value once. So, this algorithm is faster than the old one, and keeps the T_2 spectrum continuous. This algorithm overcomes the following weaknesses of the old one: cannot be used to low SNR, large calculation and non-continuous T_2 spectrum. Except for the influence of SNR to the inversed T_2 spectrum, we analyze the effects of the number of pre-assigned T_2 spectrum bins, the number of echoes in the echo trains, and the echo space T_E . The results also indicate that the inversions of the new algorithm are very good for shale reservoirs.

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P-04

STRUCTURAL PROPERTIES AND INTERDEPENDENCES OF 1D AND 2D RELAXATION SPECTRA

Stéphane RODTS¹, Dimitri BYTCHENKOFF²

¹Laboratoire Navier - Université Paris Est, Champs sur Marne, France ²LEMMA, Nancy Université, France

Two-dimensional (2D) NMR-relaxation spectra are known to improve the identification of fluid components in complex systems, and to allow the study of interstitial fluid diffusion in porous media by correlating various relaxation processes. The question of their form has given rise to numerous conjectures. Aside, the practical calculation of these spectra is a notoriously ill-conditioned problem. In the most commonly used algorithm [1], numerical stability is obtained under strong *a priori* assumptions, namely some degree of smoothness and non negativity, which were actually shown to be spurious in the most general case [2]. Elucidating general and reliable spectral properties then seems a prerequisite for the design of new algorithms.

In this work, relaxation eigenmode formalism [3] is used to establish a number of rigorous mathematical properties about signs and intensities of the diagonal and cross-peaks in spectra obtained by various 1D and 2D NMR-relaxation techniques. It also reveals symmetries of the spectra and uncover interdependences between them. Furthermore, the approach can be made specific to porous systems through the eigenmode perturbation theory and the first-order two-site exchange model [4]. Additional properties are found, and a classification of 'exchange squares' in 2D spectra is proposed [5].

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P-05

A FAST NMR APPROACH TO EVALUATE THE VISCOSITY OF FLUIDS IN DOWNHOLE

Feng Deng, Lizhi Xiao, Guangzhi Liao

China university of petroleum, Beijing, Beijing, China

The rapid prediction the viscosity of heavy oil reservoir fluid has important significance for petroleum exploitation and transportation, and NMR techniques are able to link viscosity to measured relaxation times. This paper proposes a viscosity of crude oil prediction method using rapid two-dimensional (2D) T_1 - T_2 measurements - Driven-Equilibrium Fast-Inversion-Recovery (DEFIR) pulse sequence. The 2D T_1 - T_2 distribution is obtained only by two scans with DEFIR sequence. The effect of molecular correlation time distributions present in viscous oils is simulated and quantified. Relaxation times of intermediate viscosity dead oils show a linear correlation with viscosity on a log-log plot. This is illustrated using NMR and viscosity data from the literature [1]. Our theoretical study leads to a model based on the detected molecular motions in the fluid, that take into account distribution effects and measurement problems. Connect this work with rapid 2D relaxation times measurements, a new NMR methodology is proposed to predict viscosity more quickly and more accurately. It has been tested on our produced NMR fluid analysis system [2].

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P-06

TOWARDS MODEL-FREE ESTIMATION OF MEMBRANE PERMEABILITY IN BIOLOGICAL SAMPLES

Bernard Siow^{1,2}, Penny Hubbard³, Angela d'Esposito², Mark Lythgoe², Daniel Alexander¹

¹Microstructure Imaging Group, Centre for Medical Imaging Computing, UCL, London, UK, ²Centre for Advanced Biomedical Imaging, University College London, London, UK, ³Centre for Imaging Science, University of Manchester, Manchester, UK

The permeability of membranes within tissue microstructure is abnormal in a number of pathologies, for example in cancer¹ and stroke². We demonstrate the use of diffusion-diffusion exchange spectroscopy in yeast and diffusion-diffusion exchange spectroscopic imaging (DEXSI) in an ex-vivo rat brain on a 9.4T Agilent small bore scanner.

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We adapt the Diffusion-diffusion Exchange Spectroscopy (DEXSY)^{3,4} NMR technique for MRI of biological samples to quantify permeability. Previous studies that estimate permeability have adapted the Karger framework⁵ using biophysical models of tissue. An alternative, phenomenological approach, Filter Exchange Imaging (FEXI) has been used to quantify permeability in the human brain⁶. The FEXI study assumed a two site system and that the rate of exchange between sites was mono-exponential. A recent study suggests white matter can be better described by at least three compartments⁷. Diffusion-diffusion exchange techniques are inherently able to detect multiple diffusivities and thus the exchange of water between them. Future work will decrease total acquisition time by fast imaging and optimising the diffusion protocol⁸.

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P-07

TRAVELING WAVE MAGNETIC PARTICLE IMAGING FOR DETERMINING THE IRON-DISTRIBUTION IN ROCK

Patrick Voge^{1,2}, Martin Rückert^{1,3}, Peter Klauer^{1,3}, Walter Kullmann³, Peter Jakob³, Volker Behr¹

¹Experimental Physics 5 (Biophysics), Würzburg, Germany, ²Research Center for Magnetic Resonance Bavaria e.V. (MRB), Würzburg, Germany, ³Institute of Medical Engineering, Würzburg-Schweinfurt, Germany

Magnetic Particle Imaging (MPI) was firstly published in 2005 [1]. It is based on the nonlinear response of ferro- and superparamagnetic materials to varying magnetic fields. For imaging a field free point (FFP) with a strong gradient on the order of 1-7 T/m is moved through the sample. Only in the vicinity of the FFP a MPI signal can be detected. Sufficiently far from the FFP (depending of the gradient strength) the particles saturate and signal generation is suppressed.

A novel scanner design, the traveling wave MPI, uses a dynamic linear gradient array (dLGA) for the generation of a strong gradient. The dLGA contains 16 single coil elements, which can be driven individually, and allow the generation of a FFP with a strong magnetic gradient. This FFP can be moved linearly along the symmetry axis of the dLGA as part of a traveling wave [2]. Two additional saddle coil systems, which generate a magnetic field perpendicular to the main field, can arbitrarily shift the FFP through the field of view (FOV). In this case the FFP is moved on a sinusoidal trajectory along a 2D slice [3]. For covering a whole 3D volume the 2D slice is gradually rotated by a specific angle.

A piece of rock containing ferrous areas was scanned using this radial slice-scanning method (rSSM) by rotating the sample manually. After a slice-by-slice deconvolution using Wiener filter and a re-gridding of the datasets in a second step the

distribution of ferromagnetic material inside the sample can be reconstructed using radon transformation.

In this preliminary test the feasibility of determining the iron-distribution in stones using the TWMPI method could be shown. For comparison a measurement using a micro-CT device (220 kV) was performed, which shows similar structures inside the rock, but at the moment a quantitative validation is missing.

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P-08

RECONSTRUCTING HIGHLY UNDERSAMPLED MR IMAGE BY PATTERN RECOGNITION ALGORITHM

Fangrong Zong^{1,2}, Marcel Nogueira d' Eurydice^{1,2}, Petrik Galvosas^{1,2}

¹Victoria University of Wellington, Wellington, New Zealand, ²MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand

The acquisition of full k-space data can be time consuming, reducing the speed of magnetic resonance imaging (MRI) and increasing motion effects in clinical imaging. One alternative approach is to randomly undersample k-space data, and apply compressive Sensing (CS) technique to reconstruct the images in different sparse transform domain [1][2]. Principle Component Analysis (PCA) relies on sufficient prior knowledge/data and is widely used in pattern recognition[3]. Recently, this method was applied to image reconstruction of undersampled MRI data, by using the main principle components which are linked to corresponding large projection coefficients[4]. However, this approach requires a certain threshold, leading to the suppression of particular image features during data processing.

Herein, a new reconstruction method based on the pattern recognition is proposed to improve the image quality during PCA-CS reconstruction. Randomly undersampled data were acquired with Cartesian phase encoding in k-space. Subsequently, the projection coefficients of this image were calculated using the principle components basis. A set of images in the database were chosen, of which the projection coefficients had minimal Euclidean distances to the coefficients of the sparse-sampled image. Then this set of images was used to complement (and fill) the undersampled k-space data of the image under study. The above procedure was applied repeatedly until the results converge to a stable solution. The performance of the proposed method was evaluated for biological tissues and has shown better results than the PCA-CS reconstruction so far.

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P-09

OPTIMIZING LOW-FREQUENCY NMR MEASUREMENTS

Soumyajit Mandal

Schlumberger, Cambridge, USA

Many NMR measurements of porous media are conducted at low field strengths to reduce the effect of internal field gradients, or because of the geometry of the sensor. For example, single-sided or inside-out sensors, such as those used in NMR well-logging, typically have Larmor frequencies less than 2 MHz. At such frequencies the bandwidth of a tuned and/or impedance-matched probe circuit, which is given by ω_0/Q where Q is the quality factor, is often comparable to (or smaller than) the nutation frequency ω_1 . The slow transient response of such narrow-band probes results in distorted RF pulses with long rise and fall times during transmission and distorted, time-delayed echoes during reception.

We will describe various techniques for improving the performance of such narrow-band MR systems, including methods for increasing the bandwidth of the probe during both transmission and reception. Some are well-known, such as over-coupling the transmitter circuit to the probe. Others include active feedback damping [1], which can be used to increase the receiver bandwidth without affecting its noise figure, and ultra-broadband front-end electronics using untuned sample coils [2].

We will also discuss optimal RF pulse design for further improving aspects of system performance, such as signal-to-noise ratio (SNR), robustness to sample motion, etc. [3]. Finally, we will also discuss improvements in NMR signal processing techniques.

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P-10

EXPONENTIAL ANALYSIS BY THE KRYLOV BASIS DIAGONALIZATION METHOD

Tiago Bueno Moraes, Elton Tadeu Montrazi, Tito José

Bonagamba, Claudio José Magon

São Carlos Institute of Physics - University of São Paulo, São Carlos, São Paulo, Brazil

NMR measurements of relaxation times (T_1 and T_2) and translational diffusion coefficients (D) are powerful tools for understanding liquids located in the interior of porous media. In this context, NMR is being intensely used in important basic and applied scientific and engineering areas, such as oil science (reservoir rocks) and medicine (bones). A common objective of the experimental work is the determination of the distribution of relaxation times or translational diffusion coefficients from the experimental data, which, in the case of noisy signals, consists in an ill-posed mathematical problem. Consequently, the distributions cannot be precisely determined by known algorithms. In this work we describe a new algorithm, based

on the parametric non-linear method named Krylov Basis Diagonalization Method, KBDM [1,2], developed for fitting time domain signals defined as a sum of exponentially damped sinusoids. To evaluate the feasibility of the proposed method on the determination of transverse relaxation times T_2 , NMR-CPMG experimental data were analyzed and the results extensively compared to those obtained from worldwide popularized algorithms based on the Tikhonov regularization. In contrast to regularization procedures, the output of the KBDM is not a continuous distribution of decay constants but, indeed, a "line list" composed by the parameters of M exponentials: amplitudes and decay constants. Furthermore, the number of exponentials needed to fit the data, M , is also determined by the method. Therefore, the output of the KBDM is a discrete distribution and, to generate an almost continuous distribution, as a function of decay constants, the pseudo-noise averaging method was employed [1]. Selected samples were used to demonstrate the method: artificial alumina porous media and some rock cores. For all samples, the information obtained from the experimental data is comparable to those obtained from regularization procedures. Major advantages and drawbacks of the proposed method will be discussed. Similar tools for 2-dimensional $T_1 \times T_2$, $D \times T_2$ and $T_2 \times T_2$ NMR correlation methods are under development.

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P-11

INVESTIGATING MORE REALISTIC PORES IN DIFFUSION NMR

Bahman Ghadirian, Allan M. Torres, Benjamin Moroney, William S. Price

University of Western Sydney, Campbelltown, Australia

Pulsed gradient spin-echo based (PGSE) NMR diffusion experiments [1] can be very useful in probing the structure of microscopic pores. For example, in biological cells [2] and polystyrene beads [3], the decay of the NMR echo signal results in information rich diffusion-diffraction like patterns which directly reflect the pore dimension and shape.

However, the existing models used in analysing NMR restricted diffusion data are often inadequate and limited to diffusion in simple geometries such as between parallel planes, in cylinders and spheres. That is, ideal geometries that are far from those that occur in real systems. In this study, the diffusion propagators and pulsed gradient spin-echo attenuation equations are derived for various restricted geometries such as annular regions of concentric cylinders and spheres and rectangular pores [4-5]. The obtained theoretical results are compared to experimental NMR diffusion-diffraction profiles taking into account surface wall relaxation, orientation of magnetic field gradients and other factors.

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P-12

A NEW FAST TWO-DIMENSIONAL NMR MEASUREMENTS

Feng Deng, Lizhi Xiao, Fangrong Zong, Guangzhi Liao
China University of Petroleum, Beijing, China

Driven-Equilibrium Fast-Saturation-Recovery (DEF SR), as a new method for nuclear magnetic resonance (NMR) relaxation measurement based on pulse sequence in flowing fluid, is proposed. The two-dimensional functional relationship between the ratio of transverse relaxation time to longitudinal relaxation time of fluid (T_1/T_2) and T_1 distribution are obtained by means of DEF SR with only two one-dimensional measurements. The rapid measurement of relaxation characteristics for flowing fluid is achieved. A set of down-hole NMR fluid analysis system is independently designed and developed for the fluid measurement. The accuracy and practicability of DEF SR are demonstrated.

The DEF SR pulse sequence, which learned from Mitchell's work [1], consists two parts: an initial Driven-Equilibrium (DE) portion, followed by a Fast-Saturation-Recovery (FSR) portion. The DE sequence allows the repeat acquisition of a spectrum without having to wait for the spins to recover on the longitudinal axis. This is achieved by applying two 180° RF pulse after a free induction decay (FID). Repeat this process, the final magnetization vector tends to an equilibrium value M_{eq} which contains both the information of T_1 and T_2 of sample. The value of T_1/T_2 can be directly calculated by M_{eq} , this ratio combined with the T_1 distribution which measured by FSR pulse sequences, can obtain the T_1/T_2 - T_1 distribution. Since the DEF SR sequence is a one-dimensional experiment, the T_1/T_2 ratio distribution can be acquired in two scans. The 2D relaxation measurement is much more faster with DEF SR pulse sequence than the conventional T_1 -encoding pulse sequence. The measurement of T_2 , which is quite sensitive to molecular diffusion, is replaced by that of T_1 which insensitive to molecular diffusion. DEF SR pulse sequence is effectively applied in the measurement of NMR relaxation under flowing state.

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P-14

INVESTIGATING EFFECTS FROM RESTRICTED DIFFUSION IN MULTI-COMPONENT DIFFUSION DATA

Tina Pavlin, John Georg Seland
University of Bergen, Bergen, Norway

Heterogeneous systems are encountered both in petro physical NMR and in biomedical MRI. In such systems multiple diffusion coefficients can be detected, which potentially can be assigned to different diffusion domains. However, when high

values of the gradient strength are applied, this may introduce contributions from restricted diffusion to the experimental diffusion attenuated signal, leading to erroneous results [1]. We have investigated model systems where effects from non-Gaussian restricted diffusion can be separated from effects caused by multiple diffusion coefficients. We apply various models to analyze the experimental data, and discuss pros and cons of the different approaches.

We used a combined diffusion- T_2 (D- T_2) measurement and analysis technique [2,3]. Water saturated close packing of mono-sized (100 μm) beads represented diffusion domains with potentially non-Gaussian, time-dependent behavior. One of the samples contained polystyrene (PS) beads ($T_2=1800$ ms), and another contained glass beads ($T_2=60$ ms). This gives the same diffusion behavior, but different relaxation properties in these two samples. Two white oils (ExxonMobil), Marcol 52 ($D\approx 1\times 10^{-10}$ m^2s^{-1} , $T_2=315$ ms) and Marcol 152 ($D\approx 2\times 10^{-11}$ m^2s^{-1} , $T_2=120$ ms) represented domains with Gaussian behavior, but with lower diffusion, and with different relaxation properties. These 4 samples were prepared in small separate containers (MAS rotors). The containers were stacked inside an ordinary 5 mm NMR tube, allowing measurements on a single sample or on two samples together.

An analysis based on multiexponential models was not able to correctly account for effects caused by restricted diffusion in a system with multicomponent diffusion. However, an analysis based on separating components due to differences in dynamic behavior prior to the diffusion analysis [4] (T_2 -filter or D-filter) combined with the second cumulant approximation [5] was more accurate with respect to effects from restricted diffusion in a situation with multicomponent diffusion.

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P-15

EMERGING TECHNIQUES FOR NMR CHARACTERISATION OF COMPLEX FLUIDS

Timothy Brox, Stefan Kuczera, Bradley Douglass, Petrik Galvosas

MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington, New Zealand

In many porous systems the pore space is filled with non-Newtonian, multicomponent or viscoelastic fluids which can exhibit a wide variety of flow characteristics depending on imposed shear[1]. For instance, blood found in the matrix of biological tissue is a suspension of red blood cells in serum, a viscoelastic fluid. Numerous fluids used in the petrochemical industry, in addition to extracted resources, are multicomponent fluids which exhibit a range of wetting and permeability conditions due to their shear dependent properties. Additionally, many complex fluids may themselves form 'soft' porous materials due to internal structure, such as micelle structures formed by surfactant molecules or the

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cross-linked network in gels. Porous media research strives to understand not only the physical environment of a pore, but also the interactions between the matrix structure and the fluid that fills its voids. This research describes new techniques to utilise NMR in characterising the rheology of complex fluids prior to *in situ* porous media studies, a field known as rheo-NMR[2].

Here we present an advanced rheo-NMR hardware kit for a wide bore superconducting magnet which allows for a wider range of shear experiments compared to current commercially available hardware. One device has an integrated torque sensor safe for use inside the bore of a superconducting magnet and allows for simultaneous rheologic measurements and NMR experiments. Additionally, a second device allows for oscillatory shear and start-up profile experiments.

Finally, we recognise that, to date, rheo-NMR techniques have been applied to high field magnets while research in certain porous materials (e.g. geologic samples) typically utilises low field NMR to avoid susceptibility artifacts. Due to the recent construction of a three axis gradient set for a 2 MHz Magritek Rock Core Analyzer, we are exploring the feasibility of studying complex fluids under flow without the need for a traditional micro-imaging NMR set-up. With the development of new hardware and pulse sequences we look to bring the utility of rheo-NMR to low field NMR systems.

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P-16

MULTIFREQUENCY NMR RELAXOMETRY. NEW TECHNOLOGY AND INSTRUMENTAL PLATFORMS FOR THE EXPLOITATION OF THE FIELD-DEPENDENCE OF T1 AND T2 IN ROCK CORES ANALYSIS AND PETROLEUM APPLICATIONS

Gianni Ferrante¹, Jean Pierre Korb², Salvatore Bubici¹, Mike Mallett³

¹Stelar srl, Mede (PV), Italy, ²Ecole Polytechnique-CNRS, 91128 Palaiseau, France, ³HTS110, Lower Hutt 5040, New Zealand

Recent NMR work demonstrates that Fast Field Cycling (FFC) NMR and multi-frequency NMR relaxometry offer unique insights for study of rock cores and heavy crude oils.[1-5] Nuclear magnetic relaxation dispersion (NMRD) profiles, acquired through FFC NMR relaxometry by scanning a wide range of magnetic fields, provides unique information on the surface dynamics of confined petroleum fluids in porous rocks, thus information on “wettability” and pore connectivity in carbonates can be obtained.[1-5]

T1 distribution dispersions of crude oils as a function of the relaxation field is a powerful new technique to study asphaltene aggregation not only in model systems, but directly in heavy crude oils of various compositions.[2] Such information, obtained only with FFC NMR technique, provides important insights into highly complex fractions of crude oil and the related aggregation phenomena.[2,3] In petro-physical contexts, knowledge of the field/frequency dependence of relaxations can improve interpretation of T1 and T2 measurements in common oilfield use, assess wettability of water in reservoir rocks [6] and improve characterization of

asphaltene aggregates (allowing oilfield operations to avoid asphaltene related problems). [4,5]

Herein we describe how new FFC instrumentation for standard 10 mm and wide diameter samples up to 1.5” in combination with a variable-field (0-5 tesla) cryogen-free superconducting magnet was developed for rock core analysis and petroleum applications. Characterization of 1” carbonate rock cores and different crude oils, brines and complex mixtures, through acquisition of NMRD profiles from a few KHz up to 40 MHz, was possible. Using a variable field wide-bore cryogen-free superconducting magnet, complex two-dimensional T1-T2 experiments were also acquired.

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NMR RELAXOMETRY OF SCLERACTINIAN CORAL SKELETONS AND ENVIRONMENTAL CHANGES

Leonardo Brizi^{1,2}, Robert James Sidford Brown³, Zvy Dubinsky⁴, Giuseppe Falini⁵, Paola Fantazzini^{1,2}, Stefano Goffredo⁶, Manuel Mariani^{1,2}, Stefano Mengoli⁷, Luca Pasquini¹

¹Department of Physics and Astronomy, University of Bologna, Bologna, Italy, ²Centro Studi e Ricerche Enrico Fermi, Roma, Italy, ³953 W Bonita Ave, Claremont, CA, USA, ⁴The Mina and Everard Goodman Faculty of Life Sciences, Bar-Ilan University, Ramat-Gan, Israel, ⁵Department of Chemistry, University of Bologna, Bologna, Italy, ⁶Marine Science Group, Department of Biological, Geological and Environmental Sciences, Section of Biology, University of Bologna, Bologna, Italy, ⁷Management Department, University of Bologna, Bologna, Italy

In the framework of the European Project *CoralWarm* [1,2], the pore-volume structure of the skeletons of scleractinian corals from Mediterranean Sea have been analyzed with the aim to determine parameters from NMR Relaxometry useful to relate porosity and pore-size distribution to environmental conditions. The final goal is to relate structure variations to climate change. Mercury intrusion porosimetry shows wide ranges of pore radius, but the high Hg pressure could cause particle compression and rupture. The definition of a method to determine porosity and pore-size distribution in a non-invasive, non-destructive way can be of great interest. In a recent paper [3] we have demonstrated that NMR Relaxometry of clean coral skeletons, saturated with water, is an efficient tool for pore-volume structure characterization. The data obtained from CPMG sequence were inverted by UpenWin software [4] to get T_2 distributions. Parametric and non-parametric

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statistical test have been performed on two parameters extracted from T_2 distributions: the cut-off time (relaxation time in between two peaks, or the tail and the peak) and the micro-porosity (fraction of signal with relaxation times below the cut-off). Also, a multivariate analysis has been performed to check the sensitivity of micro-porosity to variations of mass and growing temperature. The results demonstrate that the NMR parameters so determined are good tools to check the sensitivity of the corals to the environmental changes.

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T2 RELAXATION TIME AND SELF DIFFUSION COEFFICIENT OF PEG AND DENDRIMER PROBES AS COMPLEMENTARY APPROACHES FOR THE INVESTIGATION OF FOOD MATRICES. EXAMPLE OF SODIUM CASEINATE DISPERSIONS AND ACID GELS

Souad Salami^{1,2}, Corinne Rondeau-Mouro^{1,2}, John van Duynhoven³, François Mariette^{1,2}

¹IRSTEA, UR TERE, Rennes, France, ²Université européenne de Bretagne, Rennes, France, ³Unilever R&D, Vlaardingen, The Netherlands

The measurement of both translational and rotational diffusion within the same matrix can, in principle, pave the way to a better understanding of the microscopic structure of a polymer network since it influences various motion and length scales. Generally, rotational diffusion is sensitive to motions that occur at the nanometer length scale and at the picosecond-to-nanosecond time scale, whereas in translational diffusion measurements, motion is measured over the millisecond-to-second time scale and over distances from tens of nanometers up to hundreds of microns. In this context, NMR techniques have the advantage of simultaneously and non-invasively measuring the translational and rotational diffusion of molecules. Sodium caseinate (SC) was chosen as a model protein to illustrate the potentiality of this complementary approach. SC has been the subject of many physico-chemical studies, because of its widespread use as a thickener, stabilizer and emulsifier of water-based industrial and commercial products. In aqueous solutions, casein molecules are present in the form of fragile star-like aggregates of ~20 nm in diameter containing ~ 4 to 6 $\frac{\text{g}_{\text{water}}}{\text{g}_{\text{casein}}}$. SC dispersions behave like model polymeric solutions, with a hyperentanglement

regime that begins above 8 g/100 g H₂O. Slow acidification of a sodium caseinate solution causes the formation of a gel. In this paper, we present T_2 relaxation and self-diffusion coefficient of a rigid dendrimer probe and a flexible PEG probe in SC dispersions and acid gels. The results show that the translational diffusion was greatly hindered in SC dispersions, and differences in the diffusion behaviour between PEG and dendrimer probes were observed after the overlap of the SC chains. In this regime, PEG diffused faster than dendrimer, which encountered greater resistance due to its fixed shape and lack of flexibility. On the contrary, the rotational mobility was much less hindered in SC dispersions at all casein concentration ranges investigated and depended on the local protein-probe friction. After coagulation, PEG and dendrimer translational diffusion was found to increase due to structural changes in the casein matrix, which resulted in the formation of large voids, whereas rotational diffusion of the probes was slightly retarded.

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WATER AND SALT INTERACTIONS IN GLUTEN, STARCH AND PASTA STUDIED WITH MULTINUCLEAR MR

Diana Bernin¹, Thomas Steglich², Magnus Röding³, Annelie Moldin⁴, Maud Langton⁵, Daniel Topgaard⁶

¹Swedish NMR Centre, Gothenburg University, Gothenburg, Sweden, ²SIK - The Swedish Institute for Food and

Biotechnology, Gothenburg, Sweden, ³Department of Mathematical Statistics, Chalmers University of Technology and Gothenburg University, Gothenburg, Sweden,

⁴Lantmännen Cerealia, Järna, Sweden, ⁵Department of Food Science, Swedish University of Agriculture Science, Uppsala, Sweden, ⁶Division of Physical Chemistry, Lund University, Lund, Sweden

Swedish University of Agriculture Science, Uppsala, Sweden, ⁶Division of Physical Chemistry, Lund University, Lund, Sweden

Salt is added to food products for its flavor, texture and preservation. Sodium ions give the salty flavor, but can cause health problems if their consumption exceeds the reference daily intake of 1.5g¹. The rule for cooking pasta is to add 7g of sodium chloride to 1l water for every 100g of pasta. To minimize the sodium intake when eating pasta dishes, it is necessary to characterize the impact of salt on cooking pasta and the interactions of salt ions with starch (polysaccharide) or gluten (protein), the main components of pasta.

¹H relaxation-weighted images were acquired during cooking gluten- and starch-rich pasta inside the spectrometer. The addition of NaCl to the cooking water seemed to slow down the water migration into pasta and thereby lengthening the cooking time.

Furthermore, the pasta was cooked in sodium fluoride solution to monitor the sodium and fluoride ion migration with ²³Na and ¹⁹F imaging. The travelled distance of both ions differed depending on the composition of the pasta for the same cooking time. For high gluten content, both ions were still located at the edge of the pasta also after 16 min cooking time in contrast to high starch content, where the ions were distributed over the whole pasta.

Binding of sodium and fluoride ions to starch or gluten was verified with ²³Na double-quantum filtered (DQF) and ¹⁹F 2D exchange spectroscopy (EXSY), respectively. DQF showed 'bound' sodium ions independent on raw material but the

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binding behavior altered upon cooking for starch compared to gluten. ¹⁹F EXSY spectrum showed cross peaks indicating slow exchange of fluoride ions in the presence of gluten in contrast to starch.

Interestingly, both positively and negatively charged ions seemed to interact with starch and gluten and thus compete with water.

¹<http://www.efsa.europa.eu/en/ndatopics/docs/ndatolerableuil.pdf> (p.429-446)

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NMR STUDY OF THE FILM FORMATION OF STARCH SOLUTIONS

Sushanta Ghoshal^{1,2}, Siegfried Stapf¹, Paul Denner¹, Carlos Mattea¹

¹Dept. of Technical Physics II, TU Ilmenau, Ilmenau, Germany,

²School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, USA

Starch is the second most abundant natural biopolymer after cellulose from plant origin which is available in various parts of a plant, such as seeds, leaves, roots, tubers and the fruit pulps. Depending on the initial concentration of starch in water during its film formation, initially, a precipitation or a white elastic gel can be formed. Film formation from the aqueous samples of 1% and 5% corn starch (w/v) was studied. Using a camera at the initial stage of drying it was observed that the 1% starch containing sample forms a precipitation at the beginning, whereas the 5% starch containing sample is a uniform gel. With evaporation, the thickness of the upper solution part of the 1% starch containing sample was reduced and the lower precipitation layer became densely packed. By the application of the CPMG pulse sequence at different layer positions, the drying process of these systems was followed using a single-sided NMR scanner. Spin-spin relaxation times (T₂) were obtained for each layer from the analysis of corresponding echo decays. From the depth dependent T₂ relaxation time study it was found that the molecular mobility of these two samples varied notably at different stages of film formation. For instance, at an intermediate stage, a gradual decrease in mobility of 1% starch containing sample towards the air-sample interface was observed although 5% starch containing sample was homogeneous all along the sample height. At a later stage of drying, heterogeneity in the dynamics was observed in both samples showing that the bottom part of the samples is less mobile than the upper part. Wide-angle X-ray diffraction was used to determine the structural homogeneity of the completely solidified films obtained from the studied samples. A mechanism is proposed to describe the observed dynamic and structural heterogeneity.

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LOW-FIELD NMR INVESTIGATION OF ENZYMATICALLY DEGRADED CARTILAGE WITH HIGH SPATIAL RESOLUTION

Erik Rössler, Carlos Mattea, Siegfried Stapf
TU Ilmenau, Dept. of Technical Physics II, Ilmenau, Germany

The layered structure of articular cartilage is reflected by a pronounced depth dependence of T₂ as a consequence of different degrees of order of the collagen fibers but also of a gradient of water and glycosaminoglycan (GAG) concentration,

respectively. The orientational order also results in an angular dependence of T₂ [1]. T₁, however, at conventional laboratory field strengths shows little variation with depth or orientation.

In this study, the dependence of relaxation times in bovine articular cartilage is investigated at 0.27 T and 0.44 T using portable scanners. Depth-dependent scans were carried out with resolutions between 20 and 100 μm as a function of sample curvature. While a systematic variation of T₂ and diffusion coefficient is found in agreement to observations at high fields, T₁ also shows a strong depth dependence that correlates with the tissue's layer structure. This effect is explained by the increased T₁ contrast commonly found towards smaller magnetic field strengths, probing slow and anisotropic molecular reorientations that dominate the relaxation dispersion at low resonance frequencies [2]. Superposed onto the dependence of T₁ are the quadrupolar dips, reduced relaxation times between about 10 and 70 mT which indicate cross-relaxation of protons with the partially immobilized nitrogen nuclei in amino acids in collagen and glycosaminoglycans (GAGs). Varying the composition, water content or structural integrity of cartilage affects both the general frequency dependence of T₁ and the shape of the quadrupolar dips, providing a possible diagnostic access to diseases such as osteoarthritis (OA). A statistical correlation between the degree of OA and the magnitude of the quadrupolar dips has been identified [3], but it remains unclear whether this dependence must be assigned to changes in the GAGs, collagen or both. In this study, the enzymatic activity of trypsin and collagenase and their influence on the relaxation dispersion in general, and the quadrupolar dips in particular, has been investigated for cartilage and its constituents.

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MOLECULAR DYNAMICS STUDIES IN POLYMERIC MICELLES USING FAST FIELD-CYCLING NMR RELAXOMETRY

Cecilia Fraenza¹, German Farrher¹, Esteban Anorado¹, Amin Ordikhani-Seyedlar², Carlos Mattea², Siegfried Stapf², Romina Glisoni³, Alejandro Sosnik³

¹Laboratorio de Relaxometría y Técnicas Especiales (LaRTE), Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba and IFEG (CONICET), Córdoba,

Argentina, ²Department of Technical Physics II / Polymer Physics, Institute of Physics, Faculty of Mathematics and Natural Science, Ilmenau University of Technology, Ilmenau, Germany, ³BIONIMED. Departamento de Tecnología Farmacéutica. Facultad de Farmacia y Bioquímica. Universidad de Buenos Aires, Buenos Aires, Argentina

Amphiphilic poly(ethylene oxide)-poly(propylene oxide) block copolymers are thermoresponsive materials that display unique aggregation properties in aqueous medium [1]. Due to their ability to form stable micellar systems in water, these materials are broadly studied for the solubilization of poorly water-soluble drugs. In this work, molecular dynamics

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of triblock copolymers (commercial name Pluronic from BASF) F68 (EO₈₀PO₂₇EO₈₀), F108 (EO₁₄₁PO₄₄EO₁₄₁), and F127 (EO₁₀₁PO₅₆EO₁₀₁) at different concentrations (10-22.5% w/v) and temperatures (3-25°C) were analyzed using fast field-cycling NMR relaxometry. The frequency range was from 8 KHz to 20 MHz, considering that the measured local field values were lower than 1 KHz for all the samples. This study was complemented with NMR spectroscopy, NMR measurements in the rotating frame, atomic force microscopy (AFM), transmission electron microscopy (TEM) and dynamic light scattering (DLS) techniques. Although proton NMR spin-lattice relaxation rate dispersions showed a weak dispersion in the laboratory frame and no dispersion in the rotating frame, they evidenced a bi-exponential behavior that has been attributed to different relaxation of PEO and PPO groups in agreement with other authors [2]. Also, it was observed that the larger the ratio *R*, defined by number of protons of PPO divided number of protons of PEO, the less evident bi-exponentiality. In this work we present experimental results and a proposed dynamical model that explains the measured relaxation dispersion curves.

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MR MEASUREMENTS OF COLLOID SUSPENSION DYNAMICS IN POROUS MEDIA

Einar O. Fridjonsson¹, Joseph D. Seymour², Sarah L. Codd³, Michael L. Johns¹

¹School of Mechanical and Chemical Engineering, University of Western Australia, Crawley, WA, Australia, ²Department of Chemical and Biological Engineering, Montana State University, Bozeman, MT, USA, ³Department of Mechanical and Industrial Engineering, Bozeman, MT, USA

Colloidal suspensions are ubiquitous, occurring in many applications of soft matter [1], drug delivery [2], filtration technology [3] and physiology (e.g. blood flow). The study of colloidal suspension dynamics is receiving renewed attention due to the flow control offered by microfluidic devices to manipulate complex fluid flows [4]. In this work we present the results of dynamic NMR experiments on colloidal suspensions flowing inside porous media.

The colloidal suspensions used in this work are mono-modal NMR active $1.25 \pm 0.46 \mu\text{m}$ radius colloidal particles prepared through an evaporative emulsion process⁵. The spherical particles have an oil-core, which allows for the spectral differentiation of the particles and the suspending fluid. The porous medium is filled with 80 - 120 μm radius spheres and investigated using high-field (300MHz Bruker superconductor) and low-field (12.9MHz Oxford Rock Core Analyser) NMR. Rheological information on the colloidal suspensions obtained from analyzing the shear-induced diffusion in a μ -capillary is extended to work on model porous medium where the change in flow field due to particle deposition is investigated using PFG-NMR. The work presented forms the framework for extension of colloidal particle dynamics investigation inside consolidated material and rock matrices using low-cost low-magnetic field NMR instruments.

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COMPACT NMR ON SIDE WITH THE SAMPLE INSIDE AND OUTSIDE

Bernhard Bluemich, Ernesto Danieli, Kawarpal Singh, Wasif Zia *RWTH Aachen University, Aachen, Germany*

Today compact NMR instruments are becoming increasingly portable. They can be moved to the site of the investigation or even carried along from place to place. We report two selected, recent applications of this technology. Application I concerns stray-field NMR measurements of relaxation decays with the profile NMR-MOUSE: these were conducted in the Chapel of St. Mary in the Royal Abbey of Chaalis. Quantitative volumetric moisture depth profiles have been acquired in water damaged original and restored wall sections. Significant variations of moisture content are observed with depth. These are compared to volume-integral, average moisture content data determined by other methods. Application II concerns high-resolution NMR spectroscopy under the fume hood for quality control of chemical compounds, analysis of hazardous chemicals, and reaction monitoring in real time. Among others, studies of mechanistic pathways and kinetics are reported for different reactions in organic synthesis, which involve protecting and deprotecting carbonyl functional groups with acetals and ketals.

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THE USE OF LOW FIELD NMR TO ILLUSTRATE CHANGES IN THE SPECIFIC SURFACE OF CHALK

Konstantina Katika, M. Monzurul Alam, Ida Lykke Fabricius *Technical University of Denmark, 2800 Lyngby, Denmark*

Nuclear Magnetic Resonance (NMR) spectrometry has proved to be a good technique for determining petrophysical properties of reservoir rocks [Kenyon, 1997]. In this study we investigate how changes in specific surface of chalk affect the NMR signal. The transverse relaxation rate, $1/T_2$ in NMR experiments is proportional to the surface to volume ratio in a homogenous porous system [Coates et al., 1999]. We compared three cases. The first experiments on outcrop chalk with high salinity brine (sodium chloride, magnesium chloride, calcium chloride and sodium sulfate) showed that saturation with divalent ions (Mg^{2+} , Ca^{2+} and SO_4^{2-}) can cause major shifts in the T_2 distribution curve, probably due to precipitation in the pore space [Katika et al. 2013]. In a second set of experiments, two types of outcrop chalk saturated with the same brines gave different NMR signals, probably as a result of different specific surface. Finally, fluid samples where precipitation took place were found to show shifts in the T_2 relaxation curve due to the creation of crystals. The results of this work could benefit the ongoing study on the optimization of the water composition

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PREDICTING THE FORMATION FACTOR AND PERMEABILITY OF POROUS MEDIA USING RADIUS BASIS FUNCTION INTERPOLATION METHOD

Yulong Zou¹, Ranhong Xie¹, Falong Hu², Chaoliu Li², Changxi Li²
¹State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China, ²Research Institute of Petroleum Exploration & Development, Beijing, China

The relationships among the physical properties of porous media usually can't be expressed analytically. Limited by the number of physical parameters that can be considered and the complexity that empirical formula can be fitted, the empirical formula sometimes can't effectively describe the relationships among physical properties. Interpolation method, provided satisfying all known experiment data, can better predict the unknown physical properties of porous media. Compared to other interpolation methods (for example kriging interpolation, etc.), radius basis function (RBF) interpolation method can perform multivariate interpolation and have no limitation in dimension. So, RBF can consider as much as possible the influence of the related physical properties that are related to the physical properties being predicted. The related physical properties can be either scalars or vectors. In this paper, RBF was used to construct the expressions between porosity and formation factor, and between nuclear magnetic resonance T_2 distribution and permeability. The effectiveness and advantage of RBF were verified by comparing the predicted values from RBF method with the measurements. RBF interpolation method could become the research focus of evaluating porous formation and determining rock physical parameter.

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DETERMINING PORE LENGTH SCALE OF ROCKS USING DIFFUSION EIGENMODES IN 2 MHZ ROCK CORE ANALYZER

Huabing Liu^{1,2}, Marcel Nogueira d' Eurydice^{1,2}, Sergei Obruchkov^{1,2}, Petrik Galvosas^{1,2}

¹Victoria University of Wellington, Wellington, New Zealand, ²MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand

The theory of eigenmodes of spin diffusion was first proposed to explain the multi-exponential decay in porous media with uniform pore size [1]. The lowest eigenmode ($n = 0$) governs spin-lattice/spin-spin relaxation and its eigenvalue relates to the pore length, a , and the surface relaxivity, ρ . On the other hand, the eigenvalues of higher eigenmodes ($n > 1$) are functions only dependent on the pore length, a , although the relative magnitudes are normally one order of magnitude smaller than the lowest mode. One efficient method to enhance the contributions from the higher eigenmodes was developed in the presence of spatially bounded internal magnetic field B_{in} [2, 3]. This technique has been used as a reliable tool to determine pore length distributions at high-field, for rocks [4], concretes [5] and biological tissues [6, 7].

Low-field NMR technology has gained extensive acceptance as a petrophysical approach for evaluation of reservoir properties. However, the contributions from higher eigenmodes are mostly hidden because of the relatively weak inhomogeneity of the internal magnetic field B_{in} . To this extent, higher eigenmodes were excited with optimized encoding periods and utilized to probe pore length scales of sandstone and limestone using a 2 MHz Rock Core Analyzer [8]. The results were confirmed by comparison with measurements performed in a 64 MHz NMR system, which supports that detection of pore length scales is feasible at low-field.

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QUANTITATIVE-MRI TESTS ON FLUORINATED COMPOUNDS TO PRESERVE CULTURAL HERITAGE POROUS MEDIA AND SAFE FOR THE ENVIRONMENT

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Villiam Bortolotti^{1,6}, Leonardo Brizi^{2,3}, Robert J.S. Brown⁴, Mara Camaiti^{5,3}, Paola Fantazzini^{2,3}, Manuel Mariani^{2,3}, Marianna Vannini^{1,6}

¹DICAM, University of Bologna, Bologna, Italy, ²Department of Physics and Astronomy, University of Bologna, Bologna, Italy, ³Centro Studi e Ricerche Enrico Fermi, Roma, Italy, ⁴953 W Bonita Ave, Claremont CA, USA, ⁵IGG-CNR Section of Florence, Firenze, Italy, ⁶Interdepartmental centres of industrial research "Energy and Environment", Operative Unit "Industrial Ecodesign, waste recycle and life cycle of products", Rimini, Italy

The internal distribution of water-repellent products applied to surfaces to make a porous material repellent is of great interest in the field of the safeguard of cultural heritage items such as stone buildings, statues and frescos. Water is the main cause of degradation of porous materials exposed to rain, moisture and air pollutants. In previous papers,¹ it has been shown how MRI allows one to evaluate and compare the performance of products and treatments used. Those products were commercial ones, made for different uses than cultural heritage items protection. In the middle of the '80s, the group of CNR in Florence started to synthesize mono-bi- and tetra-functionalized perfluoropolyetheric compounds for the specific use in the protection of stone, with the following properties: (i) stable to chemical agents, heating and UV irradiation; (ii) high water-repellency; (iii) ability to perform treatments in such a way that the natural permeability of stone to air and water vapor is not significantly reduced; (iii) chemically inert with the stone substrate, and therefore completely reversible. Unfortunately, the best products synthesized were soluble in chlorofluorocarbons.

Now, new products containing a perfluoropolyetheric block have been synthesized. They are soluble in alcohols and hydro-alcoholic solvents, but not soluble in water or chlorofluorocarbons. Their hydrophobic and penetration properties have been investigated by MRI images, taken on biocalcarene samples treated with commercial and new fluorinated compounds, at increasing times during capillary water absorption. The presence of water inside each sample could be visualized and the height reached by the wetting front quantified as a function of time. The images were analyzed by an in-house software able to identify the front by an objective criterion. The images show the different protection efficiency of products and treatments. Good fits to the data were obtained with theoretical and empirical models of absorption kinetics, starting from the Washburn model. The data analysis gives us parameters useful to quantify the effects of the treatments on the capillary properties. The results demonstrate the better performance of the new fluorinated compounds able to preserve stones and environment.

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RELAXATION MEASUREMENTS OF SPECIFIC SURFACE AREA IN SILICATE POROUS MEDIA

Oleg Kishenkov, Alexander Perepukhov, Alexander Maximych, Dmitry Alexandrov
Moscow Institute of Physics and Technology, Moscow, Russia

The use of NMR relaxation for the determination of porous

media SSA is based on the measurement of the T_1 and T_2 relaxation times of the pore fluid. In the fast diffusion limit $1/T_{1,2} = 1/T_{1,2,b} + \rho_{1,2} S/V$, where $T_{1,2,b}$ denotes bulk relaxation times and S/V – the surface-to-volume ratio. Longitudinal and transverse relaxivities ρ_1 and ρ_2 depend on the physical and chemical properties of the fluid and the pore material [1].

If β_{bulk} is the porous medium bulk density, β_{grain} – the solid density and $d = V/S$ – the pore caliber, its SSA is $S_m = (1/\beta_{\text{bulk}} - 1/\beta_{\text{grain}}) \sum_i (\rho_i/d_i)$, where ρ_i is the volume fraction of the d_i -caliber pores, $d_i = V/S_i$. The $\sum_i (\rho_i/d_i)$ is calculated on the basis of the pore size distribution of the sample and gauge coefficients ρ_1 and ρ_2 , acquired by means of model porous media.

The T_1 and T_2 of water and hydrocarbons have been measured in phantoms, made of homogenous glass beads with diameters ranging from 57 μm to 436 μm and a quartz sand sample. The SSA has been calculated from the relaxation data and compared to the SSA measured by BET method [2].

It has been found that the water $\rho_1 = 3.1 \cdot 10^{-3} \text{ cm} \cdot \text{s}^{-1}$ is equal to its value in siliceous rocks with low clay content [3]. It proves the applicability of the glass beads as a model for silicate samples. Adsorption measurements of the sand sample SSA yields $S_m = 1.97 \pm 0.05 \text{ m}^2 \cdot \text{g}^{-1}$, which within the limits of 7 % error agrees with the relaxation $S_m = 1.965 \pm 0.15 \text{ m}^2 \cdot \text{g}^{-1}$, acquired with water and is half the decane $S_m = 3.86 \pm 0.28 \text{ m}^2 \cdot \text{g}^{-1}$. The divergence of the results is probably due to capillary action on the granular material. Thus, NMR relaxation is a robust method for the SSA measurements of silicates.

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DYNAMIC CORRELATIONS BETWEEN INHOMOGENEOUS MAGNETIC FIELDS, INTERNAL GRADIENTS, AND TRANSVERSE RELAXATION, AS A PROBE FOR PORE GEOMETRY AND HETEROGENEITY

John Georg Seland

University of Bergen, Bergen, Norway

When a porous medium is placed in a static magnetic field, a spatial inhomogeneous magnetic field, which depends on the geometry of the porous network and on the differences in magnetic susceptibilities, is generated within the media [1]. This spatial inhomogeneity of the magnetic field causes inhomogeneous line-broadening in the NMR spectrum of a confined liquid, and leads to creation of internal gradients within the sample. It is well known that the distribution of relaxation times and internal gradients within the porous media both can be related to the geometry of the system. In addition, it has been shown that different values of the spatial inhomogeneous magnetic field (i.e. different parts of the NMR spectrum) also represents water in different parts of the porous network [2,3]. In this study we have applied 2D NMR experiments where the spatial inhomogeneous magnetic field is correlated to both the internal magnetic field gradients (G_0) and the transverse relaxation time (T_2). This enables us to obtain more localized information about the geometry of

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the porous network.

The experiments were performed at 25 °C on a Bruker Avance 500 MHz instrument (Bruker Biospin, Ettlingen, Germany), using a commercial probe (DIFF30). The experiments were performed on different types of close packings of glass beads, all saturated with distilled water. Sample 1 contained mono-sized spheres with a size of 30 μm . Sample 2 contained mono-sized spheres with a size of 100 μm . Sample 3 contained spheres with a size distribution between 5-50 μm . Sample 4 contained spheres with a size distribution between 145-165 μm .

The obtained results show that the distribution of G0 and T2 obtained for different values of the spatial inhomogeneous magnetic field can be related to the local geometry of the different samples.

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STUDY OF HYDROCARBON COMPOSITION BY NUCLEAR MAGNETIC RESONANCE (NMR)

Zijian Jia, Lizhi Xiao, Feng Deng, Guangzhi Liao
State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China

In this work we discussed how composition of oil affects relaxation and the relaxation mechanism in oil. And we focus on multidimensional spin correlation functions extracted from low field relaxation data and show how they can be used for estimating saturated, aromatic, asphaltene and resin (SARA) analysis percentage composition.

Oil NMR relaxation is mainly caused by dipole-dipole interaction. Fluid composition affects both the NMR relaxation behavior and the translational diffusion property. NMR relaxation in fluids is sensitive to molecular motion, which in turn depends on the sizes of the molecules and their mutual interactions. By analysing the T1-T2 -D maps, we may infer the compositions of heavy oil, and how they affect the relaxation.

In an attempt to isolate the effects of composition from other factors affecting relaxation and to study composition interaction in their natural environment, we systematically varied the SARA concentration in the native crude oil (i.e., in the oil from which they originated). We will show how they affect the result.

We will show the relaxation mechanism in oil and their composition mutual interactions. It is shown we can estimate the SARA percentage composition from the multi-dimensional NMR.

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PREPARATION AND NMR STUDY OF ARTIFICIAL ALUMINA POROUS MEDIA

Elton Tadeu Montrazi¹, Edson Luiz Gea Vidoto¹, Sérgio Rodrigues Fontes², Carlos Alberto Fortulan², Tito José Bonagamba¹

¹São Carlos Institute of Physics - University of São Paulo, São Carlos, São Paulo, Brazil, ²São Carlos School of Engineering - University of São Paulo, São Carlos, São Paulo, Brazil

In this work we present a method for preparing ceramic materials with controlled porosity and their characterization by NMR relaxation, mercury intrusion porosimetry (MIP), and 3D X-ray micro-computed tomography (μCT). Artificial alumina ceramics porous media were manufactured by dry pressing method, which preserves their intrinsic porosity. Additionally, it was added to the manufacturing process a pore-forming agent in order to induce bigger pores under a controlled way. Sucrose crystals were chosen as pore-forming agents and their sizes were carefully selected by using sieves. During the sintering process, these crystals were burned off, creating along the ceramic material induced pores interconnected by intrinsic pores. Two groups of samples were prepared, presenting intrinsic pore sizes of about 0.5 μm and induced pores sizes in the range of 100 to 500 μm (sample A) and 300 to 1200 μm (sample B), which were estimated by MIP and μCT . By the use of CPMG NMR pulse sequence, the following average T_2 values 0.05, 1.2, and 1.7 s were observed for water within the intrinsic and induced pores in samples A and B, respectively. From the point of view of T_2 distributions, the results observed are very consistent with sample preparation, being the average T_2 values directly proportional to the size of the intrinsic and induced pores. The obtained results validate the manufacturing process and the prepared artificial porous media are being excellent samples to be used as models for testing traditional and under development NMR pulse sequences, including one- and two-dimensional $T_2 \times T_2$ Exchange methods. For analyzing NMR data obtained from 1D and 2D $T_2 \times T_2$ Exchange experiments, we are using Bloch-McConnell equations [1,2]. Additionally, new manufacturing procedures are being developed in order to introduce well distributed paramagnetic impurities along the porous ceramic material.

Acknowledgements: University of São Paulo, FAPESP, CNPq, CAPES.

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MAGNETIC RESONANCE IMAGING OF LOW SALINITY FLOODING FOR ENHANCED OIL RECOVERY

Ming Li, Laura Romero-Zerón, Florin Marica, Bruce Balcom
University of New Brunswick, Fredericton, NB, Canada

Brine composition has an important effect on oil recovery during water flooding [1]. Low salinity water flooding (LSF) to improve oil recovery has been proposed with major projects in progress worldwide [2]. Contrary evidence exists [3] and there is no consensus on the mechanisms of LSF for enhanced oil recovery. In this work, MRI is employed to investigate the

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mechanisms of LSF for enhanced oil recovery. The “squeeze out” mechanism for Buff Berea and wettability change mechanism for Bentheimer are revealed from magnetic resonance (MR) T_2 variation. Variations of oil saturation distribution images, bulk and spatial resolved T_2 distribution profiles are acquired with different MR measurements - FID, SPRITE [4-6], CPMG and SE-SPI [7], respectively, during flooding processes. D_2O based brine is employed to distinguish oil and water in MR measurements. Homogeneity and heterogeneity of the core plugs' structures are illustrated. A good linear relationship between the area under the T_2 distribution profiles and the residual oil saturation in core plugs for both bulk and spatial resolved measurement is observed. LSF increases oil recovery for specific oil/brine/rock systems under certain pressure and temperature conditions. MR is demonstrated as a robust tool to monitor oil displacement processes and reveal changes of the petrophysics properties in core plugs during flooding.

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THE TEMPERATURE EFFECT ON CEMENT HYDRATION VIA FAST FIELD CYCLING NMR RELAXOMETRY

Codruta Badea¹, Alexandra Pop¹, Carlos Mattea², Siegfried Stapf², Ioan Ardelean¹

¹Technical University of Cluj-Napoca, Department of Physics and Chemistry, Cluj-Napoca, Romania, ²Dept. of Technical Physics II, TU Ilmenau, Ilmenau, Germany

Cement hydration is a complex and irreversible chemical reaction of cement grains with water molecules and is the basic process present in all cement-based materials. One of the most important factors influencing the normal process of ionic dissolution and thus the formation of the initial hydration products in cement based materials is the curing temperature [1]. In the case of low curing temperatures the hydrates are more homogeneously distributed which results in smaller pores and also leads to a better interconnection of different phases [1]. On the other hand, higher curing temperatures increase the coarse porosity determined by the free space between the cement grains. Consequently, the compressive strength of cement based materials decreases. The cement hydration process can be studied with various techniques, e.g. microscopy, calorimetry, electrical conductivity, etc. Beside these classical techniques, nuclear magnetic resonance (NMR) was extensively used in the last years for investigating cement-based materials. In the present work, we use the Fast Field Cycling NMR relaxometry technique [2,3] to reveal the influences introduced by different curing temperatures on early stage hydration of gray cement. Even if white cement is often preferred in the NMR studies of cement-based materials

due to the smaller internal gradient effects on experimental data, in the present work gray cement (CEM I 52.5R, Holcim, Romania) is chosen on purpose. This choice is motivated by the aim of enhancing the contribution of the paramagnetic centers located on the surface to the relaxation mechanism [2]. The evolution of the relaxation dispersion curves was monitored for different hydration times and four different curing temperatures. The experimental data were compared with a theoretical relaxation model [2,3] which allows monitoring of the capillary pores surface-to-volume ratio evolution. Moreover, information about the transverse correlation time and the surface diffusion coefficient of water molecules was extracted revealing constant values in the investigated temperature range.

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PERMEABILITY PREDICTION IMPROVEMENT USING 2D NMR DIFFUSION-T2 MAPS

Andre Souza¹, Giovanna Carneiro¹, Austin Boyd¹, Lukasz Zielinski², Martin Hurlimann³, Edmilson Rios⁴, Willian Trevizan⁴, Bernardo Santos⁴, Vinicius Machado⁴, Lawrence Schwartz³, Rodrigo Bagueira⁵

¹Schlumberger Brazil Research and Geoengineering Center, Rio de Janeiro, RJ, Brazil, ²Schlumberger Gould Research Center, Cambridge, UK, ³Schlumberger-Doll Research Center, Cambridge, MA, USA, ⁴Petrobras Research and Development Center, Rio de Janeiro, RJ, Brazil, ⁵Federal Fluminense University, Niteroi, RJ, Brazil

In complex carbonate reservoirs, NMR logs provide a lithology independent total porosity that matches core porosity better than the classic density-neutron crossplot porosity. NMR logs can also provide permeability estimations and pore size distributions. However, the presence of heavy minerals in these carbonate formations can have a significant effect on the surface relaxivity (ρ_2), the factor that scales the relationship between the transverse relaxation time (T_2) and the pore surface-to-volume ratio (S/V). Zielinski et al.¹ proposed a method for deriving ρ_2 from the two-dimensional (2D) diffusion-relaxation cross-plots maps, as an alternative to the traditional methods that correlates NMR T_2 distributions and mercury porosimetry or BET surface area measurements². This method is based on the fact that the translational self-diffusion coefficient (D) of a fluid saturating a porous media has its diffusional displacements restricted by collisions with the pore walls, so that D is dependent also on the pore size for specific diffusion times. In the present work we applied this approach for obtaining ρ_2 directly from NMR measurements and used it to improve the SDR NMR permeability estimator (kSDR). The new permeability estimator, called k_p , is proportional to the rock core porosity, the log-mean of the T_2 distribution, and the surface relaxivity parameter. We have applied this improved permeability estimation technique to an extensive set of well known benchmark quarried core samples with good results. The

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ability to acquire D-T₂ correlation maps downhole makes the k_p estimation presented here a promising new methodology for permeability estimation in heterogeneous wells where previous estimators show poor correlations.

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METHANE UPTAKE OF OIL SHALES PLUGS AT ELEVATED PRESSURES STUDIED BY NMR RELAXOMETRY

Carsten Horch¹, Frank Stallmach¹, Jin-Hong Chen², Baoyan Li², Boyang Zhang², Holger Thern³

¹Leipzig University, Leipzig, Germany, ²Baker Hughes Oilfield Services, Houston, TX, USA, ³Baker Hughes Inteq GmbH, Celle, Germany

Shale oil core samples exposed to different static elevated methane gas pressures were investigated by low-field NMR at a temperature of 26 °C. The measurements were performed in a NMR compatible home-built pressure cell made of PEEK and a low-field NMR sensor generating a magnetic field of 0.119 T (¹H resonance frequency 5.1 MHz) [1]. The oil shale samples (plugs with 1.9 cm diameter and 3 cm length) were used as received. The samples were inserted in the pressure cell and exposed to the desired methane pressure of 100, 200 and 300 bar. In order to allow for methane uptake, the samples were kept at each pressure for at least 10 days before the NMR T₂ and T₁ relaxation time measurement were started.

All relaxation time distributions show a significant peak at long relaxation times which identifies the free methane gas surrounding the plug sample in the pressure cell and a broad distribution at relaxation times from below 1 to above 100 ms, which identifies water, residual oil, and methane gas in the samples. From the transverse relaxation time measurements, the histograms of the T₂ distribution were calculated. They show that with increasing methane pressure the most significant increase in NMR signal intensity is observed in the relaxation time range of 10 to 50 ms. We attribute this relaxation time range to the methane uptake of these oil shale samples. We assume that dissolution of methane in the oil components is the predominant process for methane uptake in our samples. It decreases the oil viscosity and increases the NMR signal contribution in proportion to the methane uptake. The quantitative analysis of the T₂ relaxation time histograms was used to estimate the total methane uptake during CH₄ exposition at the three different pressures.

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ROCK-TYPING OF LAMINATED SANDSTONES BY NMR IN THE PRESENCE OF DIFFUSION COUPLING

Nader Alhwety, Nawaf Sayedakram, Igor Shikhov, Christoph Arns

The University of New South Wales, Sydney, NSW, Australia

NMR measurements are widely used in the petroleum industry to determine petrophysical properties such as porosity, permeability, fluid typing and their mobility estimates. The interpretation of NMR responses from saturated heterogeneous rocks in the presence of restricted diffusion is a long standing problem in formation evaluation [1]. Diffusion coupling refers to magnetization exchange between connected pores. In such condition, the main assumption necessary to relate a relaxation rate to pore size is lost. For materials strongly affected by diffusion coupling, the acquired relaxation time distribution reflects a complicated averaging of the pore structure which is hard to interpret [2]. Thus, understanding the conditions and factors controlling coupling processes and effects on relaxation is essential for successful interpretation of NMR petrophysical data.

In this work we illustrate through simulation the impact of diffusion coupling on NMR responses to improve the rock typing methodology. We aim to understand whether the response from the layered system can be represented as a sum of separate modes relative to each rock type (i.e. total signal is additive). The simulation model carries a sensitivity study on the NMR responses of multiple sets of two different rock type layers with various thicknesses, surface relaxivities, and bulk susceptibilities. The simulation study has proved that the total magnetization can be written in terms of the pure magnetization of each layer and an addition - the magnetization of the coupled region.

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EXPERIMENT AND SIMULATION ON NMR AND ELECTRICAL MEASUREMENTS ON LIÈGE CHALK

Liangmou Li, Yong Zheng, Igor Shikhov, Christoph Arns

The University of New South Wales, Sydney, NSW, Australia

Chalk is a common rock of North Sea reservoirs attracting industry by its great storage capacity. Liège chalk is known to have very similar petrophysical properties to North Sea Ekofisk chalks. Formation factor is normally obtained by electrical resistivity measurements. Alternatively, that information potentially may be assessed with the aid of NMR.

In the presence of a single fluid saturating porous medium, a series of PGSTE NMR experiments with different mixing times provides an estimate of a time at which inherently time-dependent effective diffusion coefficient becomes constant (independent from time). In this tortuosity limit, the ratio of effective and bulk self-diffusion coefficients provides a diffusion-based formation factor estimate. However, this estimate is valid only if the response from diffusing spins is averaged, i.e. the medium is sufficiently uniform at a corresponding scale, and diffusion displacement scale is sufficiently longer than the average cluster size. [1]

To assess the similarity between electrical and diffusion

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tortuosity we constructed two distinct models, one using three different particles sizes, the other uses a Gaussian random field with two distinct particles. We simulated NMR experiments on the models to obtain the time-dependent diffusion coefficient. This provides us with diffusion-based formation factor (in assumption of a strong correlation between formation factor and tortuosity through constant cementation exponent and a known porosity). In addition, we obtained a numerically simulated resistivity-based formation factor (on a model structure). We have shown both numerically and experimentally that for Liège chalk, the formation factors measured by diffusion in the tortuosity limit and electrically do agree.

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EFFECTS OF CONFINEMENT AND STRAIN IN OPTICALLY PUMPED NUCLEAR MAGNETIC RESONANCE IN GAAS QUANTUM WELLS

Ryan Wood¹, Dipta Saha¹, Christopher Stanton¹, Phil Kuhns², Steven McGill², Arneil Reyes², Sophia Hayes³, Clifford Bowers¹
¹University of Florida, Gainesville, USA, ²National High Magnetic Field Laboratory, Tallahassee, USA, ³Washington University, St Louis, USA

The photon energy dependence of optically pumped NMR (OPNMR) was studied in GaAs multiple quantum well (MQW) samples. Data were acquired at 3.9, 4.9, and 9.4 T with circular and linearly polarized light. The OPNMR photon energy dependence is compared to the calculated electron spin polarization, allowing the peaks in the data to be assigned to specific optical transitions. Two MQW samples were studied. Sample #1 (EA-124) consists of 21 GaAs wells (30 nm well width) separated by 360 nm wide Al_{0.1}Ga_{0.9}As barriers. A 2D electron density of $\sim 7 \times 10^{10} \text{ cm}^{-2}$ was obtained by Si- δ -doping in the center of the barriers. The MQW film is epoxy bonded to a Si support. Sample #2 is an undoped 60-well multiple quantum well sample of Al_{0.34}Ga_{0.66}As/GaAs. Electronic band structure calculations were carried out using a modified Pidgeon-Brown model, which includes the effects of confinement, biaxial strain (in sample #1), and magnetic field. For each optical polarization, the photon energy dependence of the conduction band electron spin polarization was calculated from the spin-up and spin-down absorption coefficients as a function of the photon energy. Samples #1 exhibits a nuclear quadrupole splitting induced by strain caused by differential contraction of the thin film and the Si support to which it is epoxy bonded. We used the splitting to infer the tensile strain in the sample, which is included in the band structure calculations. Qualitative agreement between the calculated spin polarization and the experimental OPNMR data is obtained. The first few peaks in the OPNMR energy dependence that could be assigned to specific optical transitions are tabulated. Notably, a $\sim 5 \text{ meV}$ strain-induced light hole/heavy hole splitting is observed in both samples. Consistent with theory, strain has the effect of sharpening the peaks in the OPNMR photon energy dependence. This is because the degeneracy of the light hole/heavy hole splitting is lifted, resulting in higher electron spin

polarization and higher OPNMR enhancement. With the aid of theory, the evidence of quantum confinement effects can also be discerned in the data.

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HEAT STORAGE BY HYDRATION-DEHYDRATION OF $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Pim Donkers^{1,2}, Leo Pel², Olaf Adan²

¹M2i, Delft, The Netherlands, ²Eindhoven University of Technology, Eindhoven, The Netherlands

Systems that buffer heat are needed to match the demand and supply of renewable energy like solar heat panels. A promising system is based on hydrates of salt[1]. A major advantage is the long time storage and the reversibility of the reaction: an ideal heat battery. The heat density in such systems can be in the order of 500 kWh/m³.

In this study, we measured the dehydration reactions of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. To follow this hydration-dehydration process in real time, NMR experiments at temperatures up to 160°C are necessary. The challenge of measuring this process is even larger, because of the short relaxation times ($< 100 \mu\text{s}$) in combination with the slow diffusion coefficient of the lattice water ($< 10^{-12} \text{ m}^2\text{s}^{-1}$). For these experiments a special setup was designed with a maximum working temperature of 160°C and a static gradient up to 30 T/m. The RF-coil has a 180° pulse time of 10 μs and with a dead time of less than 10 μs , it can measure echo times of 50 μs .

Dehydration experiments with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are performed with varied heating rates and grain sizes. The total signal curve is in agreement with thermal gravimetric analysis and can be divided, based on T_2 relaxation times in two dominant relaxation times. Based on the measurements these relaxation times can be attributed to lattice water and to pore water. These pores are being generated during the dehydration process. Additionally the diffusion coefficient of the different components was measured during dehydration, giving a complete picture of the dehydration process. We observed during these experiments at transition temperatures a fast increase of pore water, indicating the formation of a porous structure and a strong discontinuity in the diffusion coefficient of the pore water component. This data is being used to model the dehydration process of crystals.

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STUDY ON NMR TEMPERATURE CHARACTER OF CRUDE OIL

Zhang Yingli, Yang Peiqiang

Shanghai Niumag Corporation, Shanghai, China

23MHz low field NMR instrument was used to analyze the 1H transverse relaxation of crude oil at different temperature. Four kinds of crude oil were measured, which were extracted from one kind of shale and three kinds of sandstones respectively. The NMR system (produced by Shanghai Niumag Corporation) was equipped with a temperature control device allowing for $\pm 0.1^\circ$ temperature regulation. The measurement temperature changed from 35° to 105° with the increment of 10°. T2g of

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crude oil increases as the temperature increasing because of the viscosity reduction. And the signal intensity should be decrease according to the NMR theory. But the signal intensity of shale oil increases oppositely. It is indicated that we can't detect the whole signal produced by shale oil at a normal room temperature because a part of it decays so fast to catch which means we need to use high temperature when we measure fresh shale rocks. And the proper temperature should be more than 75° when the signal doesn't increase obviously.

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EXPERIMENTAL AND NUMERICAL ANALYSIS FOR AUSTENITIC STAINLESS STEEL MEMBRANE STRUCTURE FOR LIQUEFIED NATURAL GAS(LNG) CARRIER CARGO CONTAINMENT SYSTEM

Jeong-Hyeon Kim, Myung-Soo Kim, Jae-Myung Lee
Pusan National University, Busan, Republic of Korea

Corrugated austenitic stainless steel sheets are used as a first barrier for the membrane type liquefied natural gas (LNG) carrier cargo containment system. Because LNG is stored at a temperature below -163°C, the safety of LNG storing systems should be ensured by selecting the appropriate structural material. The 304L austenitic stainless steel satisfies these demands; hence, it has been adopted as the most suitable material. Austenitic stainless steel, or the so-called transformation-induced plasticity steel, exhibits high material nonlinearity when strain-induced martensitic transformation especially at cryogenic temperatures. In the present study, mechanical characteristics are investigated by carrying out low-temperature tensile tests on 304L austenitic stainless steel. Moreover, a viscoplastic damage model was proposed and implemented in a user-defined material subroutine to provide a theoretical explanation of the nonlinear hardening behaviors. The verification was conducted not only by a material-based comparative study involving experimental investigations, but also by a structural application to the corrugated steel membrane of a cargo containment system for liquefied natural gas.

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CRYOGENIC MECHANICAL CHARACTERISTICS OF ALUMINUM ALLOY 5000 AND 6000 SERIES AND ITS APPLICATION TO SHIPS AND OFFSHORE PLANT

Doo-Hwan Park, Jeong-Hyeon Kim, Kwang-Jun Park, Jae-Myung Lee
Pusan National University, Busan, Republic of Korea

Aluminum alloys are used for many different fields due to its superior mechanical properties such as light weight, high strength-to-weight ratio, and excellent corrosion resistance. Among these alloys, 5000 and 6000 series of aluminum alloys have been widely adopted in shipbuilding industries in the field of helideck, hull, and primary barrier for LNG cargo containment system. In the present work, cryogenic mechanical properties of aluminum alloys were investigated at temperature (293K, 223K, 153K, and 110K) and quasi-static strain rate (10^{-2} and 10^{-4}) conditions. On the basis of experimental results, the applicability of the aluminum 5000 and 6000 series to ship and of offshore plant industries including the liquefied natural gas(LNG) carrier cargo containment system was carried out.

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STUDY ON SHALE WITH SHORT TE INSTRUMENT

Zhang Yingli, Yang Peiqiang, Cai Qing
Application Department of Shanghai Niumag Corporation, Shanghai, China

Rock analysis by NMR method has been well developed these years. One can get rock porosity, permeability, wettability, saturation, pore distribution etc. through CPMG sequence with a proper time of echo (TE). However, the TE value in commercial use is more than 300 μ s, which will cause the big information loss of the shale. In this paper, we shorten TE to 60 μ s successfully by hardware modification, then do the experiment on shale. The result shows that (1) we can get the distribution of T2 (from 10 μ s to 100 μ) which is almost lost in 300 μ s-experiment. Also, (2) the porosity in 60 μ s-experiment is more accurate than the one in 300 μ s-experiment compared to weighing method. The 300 μ s-experiment will cause 20-30% loss. But the porosity in 60 μ s-experiment is almost equal to the result from weighing method.

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THE NEW APPLICATION OF LOW FIELD NMR TECHNOLOGY IN PETROLEUM EVALUATION

Peiqiang Yang, Yingli Zhang, Qing Cai
Application Department of Shanghai Niumag Corporation, Shanghai, China

In recent years, more and more exploration and development of unconventional oil and gas storage Unconventional reservoir is prominently characterized by nanometer scale pores and non-Darcy flow, which determines its differences compared with the conventional reservoir, such as oil or gas, distribution, accumulation mechanism, and drilling or production technology, etc. So, the conventional NMR technology can not satisfy with the reservoir demands. So we change the hardware and methods to develop new applications in petroleum exploration field using low-field NMR technology.

1.Nanometer Scale Calibration

Instrument: NM12 NMR analysis system from Niumag Corporation, operating at 0.28T(12MHz for 1H), was used in all low-field experiments, which were conducted in a 25mm diameter probe at (32.00 \pm 0.01)°

Sample: Shale cuttings sample

Method: Change the echo time

Results: The more TE value increasing, the more information loss in small pores. Compared with the Mercury Intrusion, Nano CT and Focused Ion Beam methods, NMR has higher resolution and can detect approximately 2nm scale pores.

2.Heavy Oil in Nanometer Pore Calibration

Instrument: MicroMR-CL NMR analysis system from Niumag Corporation, operating, which can change the temperature from 35°-180°

Sample: Shale content heavy oil

Method: Change temperature

Results: The more temperature increasing, the more signal get

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and the T2 relaxation time increasing

3. Drilling Fluid Testing

After hydrocarbon zone is penetrated, one part of the oil and gas keeps in rock samples, and the other part enters into drilling fluid. There are mud logging methods for measuring oil and gas contents in rock samples, and gas content in drilling fluid. But there is no existing method for measuring oil content in drilling fluid.

Instrument: MR-DF NMR analysis system from Niumag Corporation, operating, which were conducted in a 25mm diameter probe at (32.00±0.01)°

Sample: drilling fluid

Method: testing oil and water content of drilling fluid on difference depths

Precision: oil content more than 0.002%

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QUANTIFYING FLUID TYPES IN SHALE WITH NMR

Colleen Muir, Dragan Veselinovic, Derrick Green
Green Imaging Technologies, Fredericton, NB, Canada

The importance of understanding unconventional reservoirs has increased in recent years due to an increase in world energy demand. Oil and gas recovery from shale has played a central role in unconventional resources. Depending on the shale reservoir, the pore network of a shale consists of structural water, mobile water, oil, organic content and bitumen. It is critical to understanding the reservoir potential to know the porosity percentages of these different components.

In this work, we demonstrate how the different fluids can be distinguished using different NMR measurements. Structural water can be separated from mobile water using a simple CPMG T₂ measurement and a T₂ cutoff. As with NMR measurements on conventional reservoirs, the key is what cutoff value to use. A method to provide accurate cutoff values for shale will be discussed.

Measurement of T₂ at different T₁ values (called T₁-T₂ maps) can be used to differentiate fluid with different viscosities. In fluids with low viscosities, T₁ and T₂ are similar, but as viscosity increases T₁ and T₂ will deviate.^[1] Organic content such as kerogen and bitumen will have much higher viscosities compared with light oil and water. This work will show how water, organic content and bitumen can be discriminated with T₁-T₂ maps in representative shale formations. Measuring T₁ and T₂ at different temperatures allows for the organic content to be differentiated from bitumen.

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P-51

INVESTIGATING HETEROGENEOUS CATALYSTS AND CATALYTIC PROCESSES USING A NEWLY DEVELOPED COMBINED MAS-NMR/RAMAN PROBE

Andrew York², Jules Camp¹, James McGregor³, Mick Mantle¹
¹University of Cambridge, Cambridge, UK, ²Johnson Matthey Tech. Centre, Reading, UK, ³University of Sheffield, Sheffield, UK

Catalysts are key in the manufacture of a vast number of chemicals, and with the drive for continually improved products along with greater process efficiency there is a need for new or improved catalysts. To allow the development of new catalysts or the optimisation of current catalysts requires a greater understanding of the materials and reactions, and the complex interactions between reactants, products, intermediates and the often multi-component catalyst materials [1]. For example characterisation of the active sites, support interactions, elucidation of the reaction mechanism, details on the reaction kinetics, etc.

Here we show the design, development and application of a magic angle spinning (MAS) NMR probe in combination with Raman spectroscopy to study both homogeneous and heterogeneous catalysed reactions. The combined technique has been applied to the study of two heterogeneous catalyst systems which are relevant in the context of this conference. The first is the methathesis of 2-pentene and ethene to 1-butene and propene over a 5% Re₂O₇/Al₂O₃ catalyst. The second reaction is the isomerization/cracking of *n*-pentane to *iso*-butane and *iso*-propane over a sulfated zirconia catalyst (8% by sulfate) catalyst. In both systems we have used ¹³C NMR to follow the reaction progress, with MAS applied in the former system, and Raman spectroscopy to simultaneously investigate the catalyst during the reaction.

We will show the combination of *in situ* NMR spectroscopy and *in situ* Raman spectroscopy has the potential to be a powerful probe of catalysts and catalytic processes, with both techniques capable of providing complementary and quantitative information on catalyst materials and on reactants, intermediates and products, thereby facilitating the development of structure-activity relationships.

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THE NMR DIP STICK

Dirk Oligschläger, Jonas Bruckhuisen, Bernhard Blümich
Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Aachen, Germany

Moisture is one of the major reasons for deterioration processes in building materials, walls and other building sites since it mediates salt crystallization, induces mold growth, and itself is able to damage the stone materials. Monitoring these processes to optimize building materials itself or to support appropriate restoration is a central task in building science. An inexpensive NMR sensor, which can be used either for permanent installation or to flexibly measure different positions at a construction site would be of high interest [1]. We present a small NMR stick of cylindrical geometry, well-suited to be used either as permanently installed sensor or as flexible tool to be used in cylindrical bore holes of walls, stones and building materials. We designed the sensor in a way similar to the Slim-Line logging tool presented by Perlo et al. [2]. The DIP (Direct Insertion Probe) stick consists of six single magnet segments with a polarization transverse to their long axis. The main difference to the Slim-Line logging sensor is the considerably smaller size (2.6 cm in diameter and 12 cm in length) and larger aspect ratio of the magnet array. We

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compensated the field homogenization effect of the dumbbell shape of the logging sensor by extending the length of the magnet array in the DIP stick. The tool was investigated in drying studies of different porous stone materials and curing of cement. Material specific constants such as drying and curing rates have been determined and characterize a certain building material. Moreover measurements at the historical Aachen cathedral were performed to show the potential use of the sensor for moisture analysis on buildings. It is planned to use the tool for studying moisture transport in a particular building site for an extended period of time.

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MR TAKES TO THE MARSHES - MR MONITORED AUTOMATED REED BED INSTALLATIONS (ARBI)

Theodore Hughes-Riley¹, Michael I. Newton¹, J. Beau Webber², Jaume Pigagaut³, Enrica Ugetti³,

Joan Garcia³ and Robert H. Morris¹

¹ *The Nottingham Trent University, Nottingham, Nottinghamshire, UK*, ² *Lab-Tools Ltd., Canterbury, Kent, UK*, ³ *Universitat Politècnica de Catalunya, Barcelona, Spain*

As part of an EU program in support of small to medium enterprises (SMES), the EU Project ARBI will enable an international consortium to develop ecologically sound and sustainable modular reed-bed installations for purifying waste-water. Magnetic resonance (NMR) installations within the reed-bed modules, monitor the clogging of the system and feed information back to the control system to constantly optimise the environment, thus maximising treatment efficiency and extending their lifecycle. The research leading to these results has received funding from the European Union's Seventh Framework Programme managed by the REA – Research Executive Agency <http://ec.europa.eu/research/rea> (FP7/2007_2013) under project reference 606326.

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EXPLORING TRANSPORT RESISTANCES IN SINGLE-FILE CHANNELS BY A COMBINATION OF HYPERPOLARIZED TRACER EXCHANGE AND HIGH-FIELD DIFFUSION NMR TECHNIQUES

Muslim Dvoyashkin¹, Hrishi Bhase¹, Navid Mirnazari¹, Aiping Wang², Sergey Vasenkov², Clifford Bowers¹

¹ *Department of Chemistry, University of Florida, Gainesville, FL, USA*, ² *Department of Chemical Engineering, University of Florida, Gainesville, FL, USA*

Confinement of guest molecules in one-dimensional channels can give rise to one of the most fascinating types of transport: single-file diffusion (SFD). SFD is expected when the nominal channel radius is smaller than the size of molecules. The signature of SFD is the proportionality between the mean square displacement (MSD) and diffusion time. Despite strong interest in this type of transport, experimental observations of

SFD in molecular single-file systems are still quite rare [1-5].

Recently we reported observations of Xe atom diffusion within L-Ala-L-Val (AV) and L-Val-L-Ala (VA) nanochannels using two independent techniques: Xe-129 pulsed field gradient (PFG) NMR and hyperpolarized Xe-129 spin tracer exchange (HSTE) NMR [5]. In both AV and VA, the time-dependence of the Xe MSD was found to be consistent with SFD. Additionally, the single-file mobility in both dipeptides was measured. Here we present a protocol for estimating the mean open channel length utilizing a model that combines input from PFG and HTSE NMR experiments. The SFD model for HTSE [3] relates the adsorbed Xe-129 signal referenced to the gas phase to the single-file mobility, spin-lattice relaxation time, and channel length. A similar relation is accessible from the standard tracer exchange model for SFD [6]. Mean open channel lengths for samples consisting of randomly oriented VA and AV single crystals, as received from Bachem, as well as a sample of pulverized AV, are determined. In each case, the open file length is found to be comparable to the typical crystallite dimension seen in SEM images. The close correspondence between these length scales leads to the conclusion that the channels in VA and AV are practically free of transport resistances.

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NMR STUDY OF IONIC LIQUIDS IN BULK AND UNDER CONFINEMENT IN POROUS MEDIA

Carlos Mattea, Amin Ordikhani, Siegfried Stapf
Technical University of Ilmenau, Institute of Physics, Ilmenau, Germany

Low-melting organic salts, commonly referred to as ionic liquids (ILs), reveal properties different from the common molecular liquids mainly due to their ionic character [1]. From both fundamental research and applications, it is important to understand the dynamical properties of ionic liquids in porous media, where the transport properties are predominantly affected by the geometrical restrictions and wall interactions.

In this contribution, diffusion and spin-lattice relaxation times (T_1) of the ILs Emim-Tf2N, Emim-BF4 and Bmim-Tf2N in bulk and confined in porous media are presented. The confinement is realized in two different media: a well characterized porous silica glass with mean nominal pore sizes of 4 nm and a porosity of 28%, and a gelatin matrix film with a mean thickness of ca. 200 μm [2, 3].

T_1 was measured at different magnetic field strength from 0.24 mT to 0.5 T and in a broad range of temperatures from 162 K to 300 K. The different ions are assessed independently by selecting either ¹H-NMR (for the cations), or ¹⁹F-NMR (for the anions). At low temperatures, evidence of decoupling of

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translational diffusion from structural relaxation [4] has been found in the bulk IL while this observation is not evident under confinement. In the latter case, the experiments reveal strong changes in the dynamics, where different ions exhibit very similar relaxation mechanisms. This may be attributed to strong cooperative dynamics in these complex liquids. The aim of this study is to assess whether the confinement, either in the rigid porous glass or in the gelatin matrix, affects the cooperative character of the molecules in this type of solvents.

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P-56

ACCESSIBLE CATALYST PORE VOLUMES, FOR WATER AND ORGANIC LIQUIDS, AS PROBED BY NMR CRYOPOROMETRY

J. Beau W. Webber^{1,2}

¹Lab-Tools Ltd., Canterbury/Kent/England, UK, ²Heriot-Watt University, Edinburgh/Scotland, UK

It is well known that porous materials such as sol-gel silicas, controlled pore glasses, templated porous materials such as SBA-15, MCM-41 and MCM-48, and zeolites offer large surface areas. This in turn makes them ideal for catalysing chemical reactions. To probe the dimensions of these pores there are a range of techniques. The scattering techniques (using neutrons or X-rays) [1] and thermodynamic techniques using gas adsorption (constant temperature) or NMR/neutron cryoporometry (constant pressure) [2,3] offer complementary methods of determining pore structure information such as pore-size distribution, surface area and pore volume.

However it is only the cryoporometric techniques that offer the possibility of directly probing the fraction of a pore that is actually accessible to a probe liquid. This fractional volume has significant impact on the catalytic efficacy of a particular solvent that is used to promote a reaction in the pores. Pore size, pore geometry, pore throat, pore surface material (hydrophilic/hydrophobic) and choice of probe liquid all influence the accessible fraction.

This change in accessible pore volume for different liquids has been known for some time, to practitioners of NMR cryoporometry [4], as well as subject to theoretical studies, but to our knowledge there have not to date been detailed systematic experimental studies using a range of porous materials and probe liquids. We have begun such a study, reported here, using sol-gel silicas, controlled pore glasses, templated porous materials such as SBA-15 and MCM-48, and zeolites, with both water and a range of organic liquids.

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INVESTIGATION OF THE EXTRACTION PROCESS IN GEL-SPINNING TECHNOLOGY OF UHMWPE FIBERS BY LOW-FIELD NMR

Meijuan Chen¹, Jingdai Wang¹, Jiang Binbo¹, Yongrong Yang¹, Siegfried Stapf², Carlos Mattea², Qingxia Gong²

¹State Key Laboratory of Chemical Engineering, Dept. of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou, China, ²Dept. of Technical Physics II, TU Ilmenau, Ilmenau, Germany

Ultra-high molecular weight polyethylene (UHMWPE) fibers display a low specific gravity and an extremely high stiffness and strength, which is about 10 times higher than steel fibers. The excellent properties of UHMWPE fibers have made them widely applied in composite materials, aviation, navigation, communication and sports.

The gel-spinning technology is the only industrial method of processing UHMWPE virgin powder with its high Tm and highly entangled molecular structure into fibers. During this process, solvent of nearly 10 times of the polymer weight is needed to disentangle the UHMWPE molecules, and consequently even more extraction solvent is required. The large amount of extraction solvent leads to high cost and environmental pollution. Besides, the details of the extraction procedure play an important role in the UHMWPE fiber productivity and performance, justifying considerable interest to investigate and optimize the extraction procedure.

The diffusion coefficient D is the key parameter in the extraction procedure. The traditional measuring method is a repeated series of weighing and drying cycles which require at least several days. Moreover, the D obtained is for the solvent-UHMWPE two component systems without any extraction solvent. Therefore, an alternative and more efficient method of determining the diffusion properties, with potential use in on-line monitoring during extraction, is of outstanding interest.

In this study, we propose to employ the NMR-MOUSE to measure the diffusion of mineral oil in the system [solvent/UHMWPE/deuterated extraction solvent] during the extraction process, thus closely mimicking the real system. It was found that the extraction solvent not only replaces and extracts the mineral oil inside what can be considered a highly porous polymer matrix, but also significantly decreases the viscosity of mineral oil. The extraction process can be described by a dual replacement/dilution mechanism. Factors affecting the extraction process were studied systematically, such as UHMWPE type, liquid-to-solid ratio, and extraction solvent. The self-diffusion coefficient measured by NMR is also used to compare the extraction efficiency, and the trends were found to be consistent with those obtained by comparing the weight loss and conventional methods of interdiffusion measurements.

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NMR STUDY OF IONIC LIQUIDS CONFINED IN GELATIN FILMS

Amin Ordikhani-Seyedlar, Siegfried Stapf, Carlos Mattea

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Department of Technical Physics II / Polymer Physics, Institute of Physics, Faculty of Mathematics and Natural Science, Ilmenau University of Technology, Ilmenau, Germany

The development of polymeric materials based on room temperature ionic liquids (RTILs) has gained considerable interest for different applications such as electrochemical actuators [REF] and highly conducting films [REF] during recent years. The combination of IL and biopolymers, like gelatin, has extended these applications in the field of biosensors as well. The structure and properties of gelatin can be manipulated by adding different types of polyelectrolyte compounds during gel formation.

In this contribution ionic liquids confined in gelatin biopolymer films were investigated with a single-sided mobile NMR scanner (0.44 T, from Magritek, New Zealand) with a strong static magnetic field gradient (920 kHz/mm). Spin-spin relaxation time (T_2) and diffusion D at different layers with microscopic resolution were determined.

Several films from solutions of different percentages of ionic liquid (from 0.75% to 5.5%) in 10% solution (wt/vol) of gelatin of 140 bloom in water, were prepared. The solution is casted and the water is allowed to evaporate until the film is ready, while the ionic liquid remains in the film because of the negligible vapor pressure that characterizes these materials.

The echo decays reveal two components in the proton signal of the films. The fast component accounts for the dynamics of the less mobile molecules of gelatine and residual water, while the confined ionic liquid is responsible for the longer component. From the diffusion measurements is found that the molecules of ionic liquid retain translational mobility. The values of the diffusion constants are smaller than the respective values in the bulk, revealing that the dynamics of the IL are restricted under confinement in the gelatin film matrix.

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NMR study of supramolecular hydrogels

M. Raue,^{1,3} A. Bernet,² M. Küppers,¹ S. Stapf,⁴ H.-W. Schmidt,² T. Mang,³ B. Blümich¹

¹ Institut für Technische und Makromolekulare Chemie, RWTH-Aachen University, Worringer Weg 1, 52074 Aachen, Germany

² Macromolecular Chemistry I, Bayreuth Institute for Macromolecular Research (BIMF), Universitätsstr. 30, 95440 Bayreuth, Germany

³ Institut für Angewandte Polymerchemie, Aachen University for Applied Science, Heinrich-Mußmann-Str. 1, 52428 Jülich, Germany

⁴ Department of Technical Physics II, Technical University Ilmenau, PO Box 100 565, 98684 Ilmenau, Germany

The ²³Na nuclear magnetic resonance (NMR) relaxometry is a non-invasive method applicable to gels and biological tissues. Supramolecular hydrogels formed by succinamic acid-based amphiphiles (**SA_n**; **n** represents the length of the alkyl chain of the amphiphiles) in saturated aqueous NaHCO₃ solution (sat. aq. NaHCO₃ sol.) are ideal model systems to monitor/investigate melting and gelation processes (Figure 1).^[1] All samples were prepared by dissolving the corresponding **SA_n** amphiphile in sat. aq. NaHCO₃ sol. at room temperature

prior to measurements (initial amphiphile concentration: 10 g L⁻¹). We could show that it is possible to estimate the effective pore size of supramolecular hydrogels based on the expanded Brownstein-Tarr model of Rijners et al. related to sodium.^[2] Our findings are in good agreement with data from differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) experiments. The establishment of such kind of measurements in the low-field NMR bears high potential for the quality-control of membranes and filters based on supramolecular hydrogels.

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MICROSCOPICALLY ANISOTROPIC SELF-DIFFUSION STUDIES IN A MACROSCOPICALLY ISOTROPIC SYSTEM

Patrick Offer, Eva Paciok, Bernhard Blümich
RWTH Aachen, Institut für Technische und Makromolekulare Chemie, 52074 Aachen, Nordrhein-Westfalen, Germany

Pulsed field gradient (PFG) NMR studies were performed on MCM-41 (Mobil Composition of Matter No. 41), which was introduced by Mobil (now ExxonMobil). MCM-41 are mesoporous inorganic silica particles which have well defined hexagonal pore geometries, which make a good model system for cylindrical pores.^[1] The pore diameter can be tuned by the use of different surfactants during the synthesis. The movement of molecules in these pores is highly anisotropic and results in an anisotropic diffusion tensor for the measured mean square displacements.^[2]

Even though the pores are anisotropic, the particles are randomly distributed, which results in an isotropic distribution of diffusion tensors. Therefore, a multi exponential signal decay can be observed in PFG diffusion measurements. A single pulsed gradient spin echo pulse sequence (S-PGSE) cannot detect the multi exponential decay, if the observed signal decay results from a distribution of isotropic pores or from randomly aligned anisotropic pores. Therefore a Double-PGSE (D-PGSE) was used to distinguish between the above mentioned cases^[3]: For a pore alignment distribution, encoding with two successive orthogonal pulses results in a more rapid decay than for the two parallel pulses. This is explained by the fact, that two orthogonal pulses include twice the number of pores with the fast diffusion direction parallel to the pulse direction of the gradients.

In the experimental data the evidence for anisotropic diffusion is revealed, by the additional signal decay for orthogonally pulsed gradients. Since these effects are second order, the differences grow larger with higher abscissa values. It is also shown, that the chronology of the pulsed gradient directions is irrelevant. It is evident from a (not depicted) data set, that only 0.3 % of all water molecules reside within the pores. This

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results in very low signal intensities. The inter particle water signal can be removed by cooling down the sample, so that the inter particle water freezes, whereas the intra particle water molecules are still in liquid state.

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FOLLOWING TRANSPORT BY MRI OF FERRIMAGNETIC NANOPARTICLES IN SAND AND SOIL COLUMN

Paméla Faure¹, Eric Michel², Stéphane Rodts¹, Stéphane Sammartino², Pierre Guillet³, Maria Neugodova², Ange Polidori³, Sophie Neveu⁴

¹Laboratoire Navier, Champs-sur-Marne, France, ²Laboratoire EMMAH, Avignon, France, ³Laboratoire IBMM, Avignon, France, ⁴Laboratoire PECSA, Paris, France

In soil, colloidal particles can vehicle adsorbed pollutant towards the groundwater or act themselves pollutants. ¹H Nuclear Magnetic Resonance allows determining soil water content by using imaging, or estimating water distribution in soil microstructure as a function of pore size by using relaxometry. It is also possible to follow water transfers in porous media (sand or soil) with profile imaging and to evaluate colloidal particle concentration by employing contrast agents. Ferrimagnetic nanoparticles, which are known to provide important contrast for NMR, have allowed us to determine the displacement of the particles in the porous media.

With the aim of comparing their transport properties, both in saturated sand columns and repacked soil cores, maghemite nanoparticles were synthesized and stabilized by adsorbing either ionic species onto their surface or neutral poly(ethylene-glycol) chains.

A minispec system operating at 0.5T was used first for measuring relaxation times (T_1 and T_2) for solution containing the sole contrast agent and then for evaluating adsorption kinetics and the effect of the adsorbed contrast agent on relaxation time. MRI measurements on sand or soil columns were performed on a vertical imaging spectrometer also operating at 0.5T. A double spin echo profile and T_1 profile sequences were used to calculate the contrast agent concentration in transport experiments.

With these two methods in hands, a series of concentration profiles of particles as a function of time was obtained. It was shown that spin-echo and T_1 profiles allow good measurements of concentration in contrast agents for sand. For soils samples additional experiments were required to determine the effect of contrast agent adsorption. These preliminary results open the door to an application of these techniques to the more challenging determination of contrast agent concentration in unsaturated sand or soil columns.

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MRI OF SLOW WATER FLOW IN POROUS MEDIA DURING INFILTRATION AND EVAPORATION BY TRACER MOTION

Sabina Haber-Pohlmeier¹, Andreas Pohlmeier², Michel Bechtold³, Natalie Schröder²

¹RWTH Aachen University, Aachen, Germany, ²Research Center Juelich, Juelich, Germany, ³Von Thünen Institut, Braunschweig, Germany

Flow processes in porous media are often too slow to be monitored by direct flow imaging. Therefore the visualization of such fluxes is best performed by tracer tracking. While T_1 reducing contrast agents are well known in medical diagnostics, their usefulness in natural porous media is not yet well explored. As pointed out in a preceding study [1], GdDTPA is most convenient since it is very stable and does not adsorb at the soil matrix. Furthermore, it's specific relaxivity in the liquid phase which is sufficiently high to yield good contrast when used in a strongly T_1 weighted pulse sequence. Here, we use a simple procedure for the quantification of tracer concentration in saturated and unsaturated natural porous media. The effects of unsaturation are compensated by a reference measurement. The procedure is applied to examples from natural porous media, which are decisive bottlenecks in the water flow from soil to the atmosphere: Root water uptake and evaporation from topsoil.

1) While plant roots take up water from the surrounding soil, GdDTPA is first enriched in the neighborhood of some roots, indicating their activity. But the tracer is also enriched in the immediate, some mm thick, layer around the root, the so-called rhizosphere, which appears dark in conventional MRI sequences. Although this layer has been frequently interpreted as water depletion zone, the enrichment of GdDTPA proves the high permeability for water and solutes.

2) During evaporation from the top of a heterogeneous porous medium enrichment of tracer is observed, followed by lateral redistribution from highly conductive to low conductive areas

[2]. Eventually a downward motion of concentrated tracer plumes against the main flux occurred, which is driven by locally increased density of tracer solution. This shows that salinization is accompanied by a more complex, dynamic behavior.

These examples illustrate the diverse applications of the method in geosciences. The discussion will be supported by results from numerical simulations by particle tracking.

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EPR IN THE IDENTIFICATION OF FE³⁺ COMPOUNDS AND FREE

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RADICALS OF SEEDS

Viviane Barbana, Daniel Valezi, Bruna Gazzoni, Priscila Veiga, Carmen Guedes, [Eduardo Di Mauro](#)
Universidade Estadual De Londrina, Londrina, Pr, Brazil

Paramagnetic species were characterized in the seeds of wild radish, rice, mustard, wheat, oats, sorghum, sunflower, soybean, cotton, beans, maize and barley by Electron Paramagnetic Resonance (EPR). Some iron complexes such as goethite (FeOOH), hematite (Fe₂O₃), magnetite (Fe₃O₄), and ferrihydrite (Fe₅HO₈·4H₂O), normally present in the soil, were also investigated by EPR, since their species can, *a priori*, be present in the seeds. The EPR experiments were performed at X-band microwave frequency (9.3 GHz) on the JEOL spectrometer (JES-PE-3X) from 77 K to 385 K and on the BRUKER spectrometer (Elexsys E-580) in a temperature range from 30 to 70 K, with the purpose of studying the thermal behavior of the species. In the EPR spectra of the seeds, it was detected the same complex of Fe³⁺ found in goethite, with $g=2.0\pm 0.2$ in all the investigated seeds. In addition, free radicals have also been detected with $g=2.004\pm 0.002$, on all seeds, and with $g = 2.013$ only in sorghum seeds. The sunflower seeds showed the highest signal intensity of the free radical. During the temperature variation, changes were observed in the spectra, in a manner that at low temperature (30 K), beyond the higher intensity on signal of the goethite and free radical, in addition, the spectra of the seeds also showed signal of hematite and traces of Mn²⁺.

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NMR FAST FIELD CYCLING INVESTIGATIONS OF UNSATURATED SOILS

[Sabina Haber-Pohlmeier](#)¹, [Siegfried Stapf](#)², [Andreas Pohlmeier](#)³
¹*Dept. of Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany,* ²*Dept. of Technical Physics II, TU Ilmenau, Ilmenau, Germany,* ³*Agrosphere Institute, IBG-3, Forschungszentrum Jülich, Jülich, Germany*

The frequency dependence of the longitudinal NMR relaxation time of unsaturated soil materials with textures ranging from pure sand to silt-loam has been investigated systematically. Relaxation time distribution functions were calculated using CONTIN from Fast Field Cycling experiments in the range from 5 kHz to 20 MHz. Sand shows monomodal relaxation time distributions, whereas for the more complex soil materials multimodal relaxation dominates which becomes also significantly faster with increasing clay and silt contents [1]. For all samples, we observed a linear dependence of the total signal amplitudes on moisture, with the exception of clayey soils, where part of the signal is lost during the dead time of the instrument. The accelerated relaxation with decreasing moisture can be explained by the Brownstein-Tarr model, if one identifies the effective pore volume with the water filled pore fraction. This is supported by the linear relation between relaxation rates and the reciprocal moisture content.

From the absence of Lorentzian spectral densities or of peaks at high Larmor frequency, and the general logarithmic dependence of relaxation times on frequency, we conclude that two-dimensional diffusion at the liquid-solid interface, which carries paramagnetic impurities, is the dominating relaxation mechanism [2]. This also holds for unsaturated soils,

which means that water remains mobile along the interfaces.

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¹H TIME DOMAIN NUCLEAR MAGNETIC RESONANCE MICROPOROSITY AND SPECIFIC SURFACE AREA OF SOILS FROM REMEDIATION SITES

[Patricia Benito](#)¹, [William Bortolotti](#)^{2,3}, [Robert J.S. Brown](#)⁶, [Leonardo Brizi](#)^{4,5}, [Paola Fantazzini](#)^{4,5}, [Giuseppe Fornasari](#)¹, [Manuel Mariani](#)^{4,5}, [Marianna Vannini](#)²

¹*Industrial Chemistry Department «Toso Montanari», University of Bologna, Italy;* ²*Interdepartmental Research Centers "Energy and Environment", Rimini, Italy;* ³*Department DICAM, University of Bologna, Italy;* ⁴*Department of Physics and Astronomy, University of Bologna, Italy;* ⁵*Centro Studi e Ricerche Enrico Fermi, Roma, Italy;* ⁶*953 W Bonita Ave, Claremont, USA*

Soil remediation has recently included the use of organic recycled materials (e.g. sewage sludge or paper mill sludge) which, thanks to their stability in aerobic conditions, can improve soil properties. Paper sludge, for example, adds nutrients to a poor Organic Matter (OM) soil, since the Total Organic Carbon (TOC) content is generally high. TOC and TOC-to-Nitrogen ratio (TOC/N) and other chemical elements (P, Ca, Mg, Na and K) are generally used to characterize amended soils [1]. It has been recently observed that the quantity of OM can influence soil texture and consequently the pore size distribution. New efforts are arising towards the use of non-invasive and non-destructive techniques to characterize this kind of sample, to gain more reliable information on interactions between OM and soil mineral phases. Proton Time-Domain Nuclear Magnetic Resonance (¹H TD-NMR) can be profitably employed to investigate the textural properties of these amended environmental substances. Applications of the TD-NMR technique are not so much used in soil science, although it shows great potential, probably due to the huge heterogeneity of these materials and to the presence of high paramagnetic ion concentrations found both in natural soils and in the contaminants. In particular, in this study contaminated soils have been characterized by T_1 distribution analysis, using a specifically developed NMR sequence to overcome experimental difficulties, to obtain information on the porosity related to the irreducible water [1]. On the other side, N_2 sorption at soils surfaces has been usually used for the determination of the Specific Surface Area (SSA). SSA depends on the structure of soil which aggregates and permits one to investigate OM-soil minerals aggregation [2]. In this work we investigate how the amount of TOC in soil sample can be investigated by TD-NMR and SSA techniques.

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¹H -NMR RELAXOMETRY AND QUANTITATIVE RELAXATION TOMOGRAPHY OF COMPOST DURING BIODEGRADATION AND MATURATION

William Bortolotti^{1,5}, Robert J.S. Brown², Leonardo Brizi^{3,4}, Manuel Mariani^{3,4}, Rosangela Spinelli⁵, Marianna Vannini^{1,5}
¹Department DICAM, University of Bologna, Italy, ²953 W Bonita Ave, Claremont, USA, ³Department of Physics and Astronomy, University of Bologna, Italy ⁴Centro Studi e Ricerche Enrico Fermi, Roma, Italy, ⁵Interdepartmental Research Centers "Energy and Environment", Rimini, Italy

The collection and composting of organic waste both from families and from industrial production processes are considered as good practices for waste management. Composts made from sewage sludge, household waste, straw, bark, have successfully been employed in gardens, pot cultures, arable land, and even in forests. In general, composts contribute to the structure and nutrient supply of soils or artificial substrates for plant growth. Compost chemical and microbial properties, which define compost maturity, are important key factors for correcting use in environmental and agricultural activities. Parameters such as the temperature, pH and C/N ratio can be observed to monitor the compost maturation and to decide on the compost quality and stability [1].

Proton Nuclear Magnetic Resonance relaxometry (¹H-NMR) can be used to follow compost biodegradation during time, as it permits the monitoring of internal compositional and structural modifications, as already observed in many food types when they experience natural or not natural processes [2]. Since generally the parameters of biodegradation are volume averaged and little is known about the influence of local behaviour on the final overall biodegradation, a local investigation of the compost mixture is desirable [3]. Quantitative Relaxation Tomography (QRT), which gives spatial information on relaxation times combining ¹H -NMR relaxometry with Magnetic Resonance Imaging, can be an innovative tool to monitor compost degradation and maturation. In this work a sample of compost has been monitored for two months by means of both T_1 and T_2 QRT maps [4]. In a first preliminary analysis, both kinds of maps seem to well describe a trend following the three phases of the composting process: mesophilic, thermophilic and maturation, moreover having information of the spatial distributions of these phases.

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LOW FIELD MAGNETIC RESONANCE FOR IN-SITU BIOREMEDIATION MONITORING

Catherine M. Kirkland¹, Randy Hiebert¹, Elliot Grunewald², David Walsh², Joseph D. Seymour¹, Sarah L. Codd¹
¹Center for Biofilm Engineering, Montana State University, Bozeman, Montana, USA, ²Vista-Clara, Inc., Seattle, Washington, USA

This research addresses the challenges associated with monitoring of the biogeochemical activity central to bioremediation of subsurface contaminants. Remediation efforts often include growth of a biofilm mat to contain or degrade chemical contaminants [1]. Previous research has indicated that nuclear magnetic resonance (NMR) is sensitive to the biogeochemical processes of biofilm growth [2] and biofilm-induced iron redox reactions which change the contaminants to an insoluble form in the subsurface [3]. Previous research conducted at MSU has shown that the Vista Clara low-field NMR spectrometer can detect biopolymers in laboratory samples of high and low susceptibility geological materials by measuring T_2 relaxation time [4].

The current research focuses on the development of low-cost NMR technology that will support 1) in-situ monitoring over space and time and 2) NMR measurement and interpretation methods to allow better monitoring of biofilm growth and geochemical remediation processes in the subsurface. We investigate laboratory experiments by placing an in-situ probe within a large-scale sand-filled bioreactor and use radial flow to stimulate biofilm growth. Successful development of this NMR technology has the potential to reduce costs and improve efficacy of monitoring subsurface remediation efforts.

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MAGNETIC RESONANCE RELAXATION MEASUREMENTS USING UNILATERAL SENSORS TO ASSESS THE CLOG STATE OF CONSTRUCTED WETLANDS

Fraser Hill-Casey, Theodore Hughes-Riley, Michael I. Newton, Robert H. Morris

Nottingham Trent University, Nottingham, UK

Constructed wetlands are a popular waste water treatment solution which have a lifespan limited by clogging which occurs throughout their operation. We have previously demonstrated the suitability of magnetic resonance relaxation measurements to determine the clog state of the gravel matrix

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in such a constructed wetland system [1-3]. In these previous studies however, various volume sensors were used to make the measurements which either required the sample to be extracted or provided a limited aperture which may have influenced the manner in which clogging occurred. In order to address these issues, in this work, we explore the possibility of making these measurements with a purpose built unilateral MR sensor. We present results from such a sensor with measurements in gravel samples from constructed wetlands in states of minimal and significant clogging. The results of T_2^{eff} , T_1 and Diffusion measurements are compared to those from a high field imaging system.

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ASSESSMENT OF APPLE TEXTURE BY QUANTITATIVE MRI

Guillaume Winisdorffer^{1,2}, Maja Musse¹, Stéphane Quéllec¹, Marc Lahaye², François Mariette¹

¹IRSTEA, TERE, Rennes, France, ²INRA, UR1268 BIA, Nantes, France

Quantitative MRI is an appropriate tool to study microstructure of intact fruit. It allows accessing multi-exponential transverse relaxation times (T_2) [1] providing insights on water status and distribution at the subcellular level and apparent microporosity maps providing information about gas distribution [2]. In this study, quantitative MRI measurements were carried out on several apple cultivars. Mechanical and biochemical analysis were also performed in order to investigate contributions of microporosity, water distribution and composition to mechanical properties characterizing fruit texture quality.

Cultivars studied were Granny-Smith, Ariane, Fuji, EC (experimental cultivar), Florina and Rome-Beauty. MRI multi-exponential T_2 and porosity were first measured with a 1.5T clinical scanner. Samples for destructive analysis were then extracted from outer parenchyma. Storage modulus (E') and dampening factor ($Tan\delta$) of the samples were measured by Dynamic Mechanical Analysis. Water and free-sugar contents and alcohol-insoluble solids were measured for all fruit. Results were analyzed using PCA and ANOVA.

The T_2 decay in all fruit was well fitted by a tri-exponential curve ($T_{21} \sim 25ms$; $T_{22} \sim 125ms$ and $T_{23} \sim 500ms$). Both T_2 and microporosity maps revealed parenchyma heterogeneity. PCA of combined MRI, compositional and mechanical data from the outer parenchyma tissue showed that 6 apple genotypes were divided into two groups: G1-Granny-Smith, Ariane and Fuji characterized by higher T_{22} , T_{23} and E' and G2-Florina, Rome-Beauty and EC with higher microporosity, $Tan\delta$ and T_{21} -associated amplitude. Apple flesh rigidity ($\sim E'$) was inversely related to microporosity.

Rome-Beauty and Florina from the G2 are known to be mealy cultivar. The results agreed with previously reported

relationship between T_2 and apple mealiness [3] and reveal a link between mealiness and $Tan\delta$.

By uncovering clear relations between apple parenchyma tissue microporosity and water status with fruit texture, quantitative MRI represents a highly valuable tool for fruit quality assessment.

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IN-SITU DETERMINATION OF SURFACE RELAXIVITIES FOR UNCONSOLIDATED SEDIMENTS

Markus Duschl¹, Petrik Galvosas², Andreas Pohlmeier¹, Harry Vereecken¹

¹Agrosphere (IBG-3), Forschungszentrum Jülich, Jülich, Germany, ²MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

The pore space structure of porous media is a key factor controlling the water flow and other properties like hydraulic conductivity. In contrast to other methods for the investigation of the pore space, NMR has the advantage to be fast and non-destructive. The easiest way to characterize the pore space by NMR is relaxometry. However, different relaxation processes contribute to the total relaxation rate in porous media which are often controlled by the surface relaxivity ρ in combination with the surface-to-volume ratio [1]. Furthermore, molecular diffusion through local magnetic field gradients may contribute to the total transverse relaxivity. These gradients are created by susceptibility differences between solid and liquid phases [2] as well as by paramagnetic impurities [3]. It is not possible to measure individually surface to volume ratios and surface relaxivities of porous media with NMR relaxometry only. However, with NMR diffusion measurements it is possible to measure the surface to volume ratio of pores without other contributions.

In our study, we show the direct determination of the surface to volume ratio of the pores using NMR diffusion measurements. We compared the results of several samples ranging from glass beads and quartz sands to soil, and pointed out the differences to gas adsorption measurements. The differences in the range of pore size distributions of our samples had different effects on NMR diffusion and gas adsorption measurements resulting in different surface to volume ratios and therefore, combined with NMR relaxometry, different surface relaxivities. Additionally, we combined NMR relaxation and diffusion measurements on goethite (FeOOH) coated sand samples with known paramagnetic content. This enabled us to isolate the additional contribution to the NMR relaxation presuming that gradients induced by paramagnetic impurities are independent of the external magnetic field strengths in contrast to gradients

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evoked by susceptibility differences.

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NUCLEAR MAGNETIC RESONANCE RELAXATION AND DIFFUSION MEASUREMENTS AS A PROXY FOR SOIL PROPERTIES

Markus Duschl¹, [Andreas Pohlmeier](#)¹, Petrik Galvosas², Harry Vereecken¹

¹*Agrosphere (IBG-3), Forschungszentrum Jülich, Jülich, Germany,* ²*MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand*

Nuclear Magnetic Resonance (NMR) relaxation and NMR diffusion measurements are two of a series of fast and non-invasive NMR applications widely used e.g. as well logging tools in petroleum exploration [1]. Applied to porous media, both relaxation and diffusion measurements depend on intrinsic properties of the media like pore size distribution, connectivity and tortuosity of the pores as well as the water saturation [2, 3]. Moreover, NMR can be used to characterize the pore space of porous media not only in consolidated sediments but also in soil.

NMR relaxation measurements provide surface to volume ratios of pores. However, these surface to volume ratios are scaled by surface relaxivities. NMR diffusion experiments on the other hand can determine the surface to volume ratios directly [4]. It is therefore possible to extract pore size and surface relaxivity individually when combining both methods. In this work, we characterized a set of sand and soil samples covering a wide range of textural classes by NMR methods. Relaxation times were monitored by the Carr-Purcell-Meiboom-Gill sequence and analyzed using inverse Laplace transformation. Apparent self-diffusion constants were detected by a 13-interval pulse sequence while varying the storage time. We correlated the results with various soil properties like texture, water retention parameters, and hydraulic conductivity. In this way, we show that we can predict soil properties based on NMR measurements and that obtained results can be used as a proxy which are based on NMR methods only.

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INVESTIGATING THE MAGNITUDE OF INTERNAL GRADIENTS IN AQUIFER SEDIMENTS

[Emily L. Fay](#), Rosemary J. Knight
Stanford University, Stanford, California, USA

Inhomogeneities in the magnetic field within a sediment can alter observed NMR relaxation and diffusion data and complicate interpretation [1,2]. Previous work shows that magnetic susceptibility contrasts between grains and pore fluids generate pore-scale magnetic field gradients in porous materials; the magnitude of these gradients are impacted

by the contrast in susceptibility, and also by pore size, pore geometry, and magnitude of the background field [3,4]. For NMR logging in aquifers, it becomes important to account for internal gradients when they are larger than the tool gradient. Existing models for predicting internal gradients are unlikely to be applicable to aquifer sediments, as the models can only be applied for simple pore geometries [5,6] or for low-susceptibility grains [1].

To assess the magnitude of the internal gradients in aquifer sediments, we measured the gradients using two NMR methods: a 2D method proposed by Sun and Dunn [7] and variable echo-spacing CPMG measurements. We looked at twelve samples from a well site in Nebraska, and six test samples prepared from clean quartz sand, magnetite grains, and hematite. To characterize the samples, we recorded bulk magnetic susceptibility, grain size distribution, and atomic composition from x-ray fluorescence. The measured gradient means in the aquifer sediments ranged from 16 G/cm to over 165 G/cm at 2 MHz. While we observed a general increase in internal gradient magnitude with increasing bulk susceptibility, the relationship appears to be complicated by additional factors.

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WATER AND PHOTOASSIMILATES TRANSPORT IN PLANTS ASSESSED BY MRI

Alena Prusova, [Edo Gerkema](#), Henk Van As
Laboratory of Biophysics, Department of Agrotechnology & Food Sciences, Wageningen University, Wageningen, The Netherlands

In plants, water and photoassimilates (sap) transport takes place in vascular tissue. There are two types of vascular tissue: xylem and phloem. Vascular tissue reflects plant ambient conditions like light intensity, water status, temperature etc. Vascular tissue, therefore, is extremely sensitive to an experimental manipulation. The effect of ambient conditions on the sap transport is, however, of a great interest. Magnetic resonance imaging (MRI) is an intact measurement technique, thus suitable for measurement of the sap transport (Van As and Duynhoven, 2013). The objective was to study the phloem and xylem sap flow velocity in tomato (*Solanum lycopersicum* L.) main stem under three light conditions: 500, 700, and 1000 mE, using home-made LED module functioning inside the MRI magnetic field. The MRI measurement was performed on three-month-old tomato plant for a continuous period of two weeks. Pulse field gradient turbo spin echo pulse sequence was used (Sheenen et al., 2000). Data were analysed by IDL

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software. The quantitative diurnal flow profiles of xylem and phloem sap flow were obtained on a per pixel basis, giving parameters of velocity, flow conducting area, and volume flow. Standard behaviour of xylem sap (Windt et al., 2007) was observed. Phloem sap velocity was almost constant during the measurement period. Phloem sap volume flow, however, was almost twice higher during the day, i.e. light on, than during the night, i.e. light off. The day-night difference of phloem sap volume flow was dependent of the light intensity. The highest day-night difference of phloem sap volume flow was observed at a light intensity of 700mE. Results showed the effect of the light intensity on the amount of the phloem sap transported via vascular tissue.

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TWO-DIMENSIONAL NMR SPECTROSCOPY ON A DESKTOP SPECTROMETER

Andrew Coy¹, Bertram Manz¹, Federico Casanova², Juan Perlo²
¹Magritek Limited, Wellington, New Zealand, ²Magritek GmbH, Aachen, Germany

Two-dimensional (2D) NMR spectroscopy is a general concept that enables chemical information to be encoded into a second dimension making use of spin-spin interactions like the J-coupling. It is particularly useful to simplify 1D spectra with overlapping signals and to identify coupled chemical groups. While 2D techniques are routinely used at high field they are not exploited on benchtop NMR spectrometer. One of the main reasons for this is the high stability required to sample the data along the indirect dimension. Frequency or phase instabilities between scans result in stripes along the t1 direction also known as t1 noise. Furthermore, the acquisition of meaningful 2D spectra is only possible if the spectrometer provides enough resolution and high signal-to-noise, otherwise the acquisition time for a 2D spectrum can become excessively long.

In this work we demonstrate the performance of 2D NMR on a 1 Tesla permanent magnet benchtop spectrometer. The magnetic field homogeneity of the magnet can be finely shimmed to achieve sub Herz resolution by means of shim coils up to order three, and high field stability is achieved by means of an external lock system. From the large variety of available 2D pulse sequences we tested the performance of J-resolved spectroscopy, correlation spectroscopy (COSY), and double quantum filtered (DQ-COSY). The results presented here demonstrate that 2D NMR is of great assistance for benchtop NMR spectroscopy where the spectrum of small molecules may appear crowded due to the strong coupling limit.

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APPLICATIONS OF A BENCHTOP NMR SPECTROMETER IN A UNIVERSITY CHEMISTRY LABORATORY

J Singh¹, V Woolner², P Northcote¹, B Manz², R Dykstra², A Coy²

¹School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand, ²Magritek Ltd, Wellington, New Zealand

In the last year, a number of companies have developed high-performance benchtop NMR spectrometers based on modern permanent magnet arrays. Unlike traditional superconducting NMR spectrometers, this new class of NMR spectrometer is sufficiently robust, safe and stable to be deployed directly in a typical chemistry laboratory and simple enough to be easily operated by students. We have been using the SpinSolve benchtop NMR spectrometer, manufactured by New Zealand company Magritek, over the last six months and report results from two different applications in our laboratory.

Chemistry in Education

Access to high-field NMR spectrometers and the cost of deuterated solvents are often cited as the main limitations to the practical use of NMR in undergraduate teaching programs. In recent times, the possibility to address this limitation has been realized with the introduction of benchtop NMR spectrometers. This paper outlines the conversion of acetophenone to *p*-nitroaniline through simple transformations typically taught in laboratory courses. NMR analysis of starting materials, reaction progress and products in native and deuterated solvents was achieved using the SpinSolve. The results of this sequence show that benchtop NMR spectrometers are suitable as a stand-alone teaching tool in the laboratory.

Isolation of Natural Products

Our laboratory employs a NMR-based protocol to screen crude extracts of marine organisms for the presence of interesting secondary metabolites. This process involves the use of 1D- and 2D-NMR experiments on a 600 MHz spectrometer. In this study, the SpinSolve was used as an alternative to screen extracts of a Tongan marine sponge for the presence of natural products. The results obtained from ¹H, COSY and J-resolved experiments were sufficient to obtain partial structure elucidation and warrant further investigation. Further purification of these extracts was also monitored by NMR and ultimately led to the identification of new and known biologically active secondary metabolites.

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¹³C ONE AND TWO-DIMENSIONAL BENCHTOP NMR SPECTROSCOPY

Bertram Manz¹, Federico Casanova², Jonathan Singh³, Hemi Cumming³, Andrew Coy¹, Juan Perlo²

¹Magritek Limited, Wellington, New Zealand, ²Magritek GmbH, Aachen, Germany, ³School of Chemical and Physical Sciences, Victoria University, Wellington, New Zealand

¹³C NMR spectroscopy is one of the most powerful analytical techniques available to organic and synthetic chemists. However access to this technology with traditional NMR spectrometers is time consuming and expensive due to the capital and operational costs of liquid-helium magnets and the location of those magnets away from the laboratories where chemists work.

In this work we demonstrate the first ¹³C NMR spectra acquired on dilute, natural abundance samples, with a benchtop NMR

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spectrometer. The magnetic field homogeneity of the 1 Tesla Halbach-array permanent magnet can be finely shimmed to achieve sub Hertz resolution on regular 5mm diameter samples by means of shim coils up to order three. Magnetic field stability is achieved by means of an external lock system. Because of the low natural abundance and gyromagnetic ratio of the ¹³C nucleus the sensitivity and stability of the spectrometer are critical to making successful measurements at the lower magnetic field strength of this magnet.

By using magnetic field shielding and temperature stabilisation the spectrometer is less sensitive to the local thermal and electromagnetic environment and can be operated routinely in a typical chemistry lab environment. One of the advantages of ¹³C NMR, compared to ¹H NMR, is the wide chemical shift dispersion which intrinsically enables a larger number of NMR peaks to be resolved. This in turn enables the elucidation of more complex molecules than with ¹H NMR at similar field strengths where peak overlap and second order coupling tend to dominate the spectra of most small molecules.

1D ¹³C methods such as DEPT have been implemented and we demonstrate both the signal enhancement and spectral editing features that are expected. We have also implemented, and report results from, a number of indirect detection 2D proton-carbon experiments, such as HSQC and HMB. The convenient availability of ¹³C NMR in a benchtop spectrometer opens the possibility for NMR to be used in a wide range of research and industrial applications where traditionally NMR is excluded because of the intrinsic mass, volume and environmentally sensitive technical characteristics of the incumbent spectrometer and liquid-helium magnet technology.

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NMR-BASED DIFFUSION LATTICE IMAGING

Frederik Laun, Tristan Kuder
German Cancer Research Center, Heidelberg, Germany

While it has been shown recently that NMR-based diffusion experiments can be used to determine the exact shape of closed pores averaged over a volume of interest [1-3], it is still an open question how much information can be gained in open systems. In this theoretical work, we show that the full structure information of periodic open systems is accessible. To this end, the so-called "SEquentialRephasing by Pulsed field-gradient Encoding N Time-intervals" (SERPENT) sequence is used [4]. The structural information is obtained by an iterative technique relying on a Gaussian envelope model of the diffusion propagator. Two solid matrices that are surrounded by an NMR-visible medium are considered: a hexagonal lattice of cylinders and a cubic lattice of triangles.

We show that a diffusion weighting with three short gradient pulses that are separated by a long time interval yield a signal which is approximately equal to a product of the form factor at different wave-vectors q . Rearranging this relation to and assuming proper initial values of the form factor, it becomes possible to iteratively determine it. Note that it is nonzero only at certain peaks reflecting the periodicity of the lattice [5].

These findings are, to our knowledge, the first description of a procedure to unambiguously reveal the structure of an open system with NMR-based diffusion experiments. We consider these findings to be foremost of theoretical interest,

which, however, - as often in physics - may pave the way to applications to more complex systems.

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QUANTIFICATION OF CHEMICAL COMPOSITION IN POROUS MEDIA USING BAYESIAN NMR

Yuting Wu, Daniel Holland, Lynn Gladden
University of Cambridge, Cambridge, UK

Being able to accurately quantify chemical composition in porous materials is a generic problem across petrophysics¹, reaction engineering² and biophysics³. In catalysis, the quantification of chemical composition in porous material can be used to better understand how the structure of a catalyst can influence the performance of heterogeneous catalytic processes. NMR spectroscopy is routinely used to characterize the chemical composition of bulk liquid samples. However, when it is extended to porous media systems, quantitative analysis is complicated by the low signal-to-noise ratio (SNR) and broad peaks caused by variations in the magnetic susceptibility. The use of low-field NMR for on plant measurements in industry would aggravate such problems. Therefore, there are strong drivers to develop techniques that can extract chemical information from relatively poor quality data.

We present a Bayesian NMR approach to quantify the chemical composition of mixtures in porous media. The performance of this general Bayesian NMR model was compared with Fourier transform (FT) analysis and was tested on ¹³C NMR data acquired on silica catalyst support saturated with mixtures of 2-butanone and cyclohexane. By exploiting prior information, the Bayesian method robustly resolves resonant frequencies that completely overlap in the FT NMR spectra. The uncertainty in the concentration estimated by Bayesian analysis decreases with increasing SNR, as expected. As an indication, the Bayesian method estimates chemical composition to within $\pm 2\%$ from data with a SNR that is too low to observe the peaks in the FT spectrum, and therefore quantitative analysis of the FT spectra is not possible. Using this new technique we demonstrate that butanone is preferentially absorbed by hydrophilic catalyst support particles, and hence the structure of the support can significantly affect reactor performance.

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