10th Bologna Conference on Magnetic Resonance in Porous Media (MRPM 10)

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Book of Abstracts

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1 Tutorial

T1 **NMR Relaxation and Petrophysical Properties**

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NMR relaxation is routinely used in the field of geosciences to give basic petrophysical properties such as porosity, pore size distribution, saturation etc. In this tutorial, we will give the basic principle used in the interpretation of the NMR signal and compare the results with other standard petrophysical techniques such as mercury pore size distribution, BET specific surface measurements, thin sections analysis and visualizations, etc.

Porosity seems a very obvious measurement. However, it relies heavily on the sample preparation and is affected by manipulation as well. When dealing with nanoporous media (coal, clays), porosity depends strongly on the instrument capabilities and mobile/non mobile protons must be distinguished.

The NMR pore size distribution is a unique information available on water saturated porous media. We will show that it can differ substantially from the distribution obtained by mercury injection for many reasons that will be detailed. In addition, transforming relaxation time (s) into pore sizes (mm) requires the knowledge of the surface relaxivity (mm/s) and we will present different methodology for its determination. The NMR pore size resolution will be discussed together with the inverse Laplace transform data processing. We will also explore the lower limit of the NMR method when considering nanometer scales encountered in clays, coals, catalysis support. Finally, we will introduce briefly recent techniques sensitive to the pore to pore diffusional exchange, providing new information on the connectivity of the pore network, but showing another possibility of discrepancy in the determination of pore size distribution with standard techniques.

T2 **NMR Diffusion Measurements of Porous Systems and the Influence of Internal Magnetic Gradients - a Tutorial Overview**

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The last three decades have seen phenomenal growth in the use of NMR diffusion measurements, also commonly referred to as pulsed gradient spin-echo (PGSE) NMR, DOSY or NMR diffusometry, to probing porous media [1-4]. Translational (or self-) diffusion is sensitive to the size and shape of a molecule and thus reports directly on whether a molecule is in some state of associa-

tion (e.g., protein-protein self-association). Thus, diffusion is a natural probe for molecular dynamics and organisation at the nanoscale. If the timescale of the measurement is such that the mean square displacement of the diffusing molecules is sufficient for the molecules to interact with any boundaries (e.g., diffusion in a porous medium or biological cell), then a diffusion measurement will provide information on the geometrical restrictions including the characteristic distances of the restriction. Further, it may also be possible to glean information on binding to and exchange through these boundaries. NMR allows diffusion to be measured without perturbing the system under study.

For NMR diffusion measurements to provide useful information it is important that the experimenter has a clear understanding of how the measurement works and of the potential sources of artifacts. This lecture will detail the theoretical underpinnings of the NMR diffusion measurements and the associated modelling needed to analyse the resulting data including the effects of distributions of the characteristic distances of restricting geometries [5]. Particular emphasis will be placed on the origins of experimental artifacts - such as internal magnetic (or background) gradients [6] which arise out of spatial differences in magnetic susceptibility that are likely to have deleterious effects on measurements in porous media.

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T3 Perspectives on Porous Media MR in Clinical MRI (Tutorial)

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Magnetic resonance in porous media and medical imaging has a history of intertwined applications; this tutorial will offer perspectives on these connections, in the spirit of recent reviews [1,2]. Many goals and challenges of research in

natural or synthetic porous media are mirrored in quantitative medical MRI. A fluid-saturated pore space might be conceptually reduced to large and small pores, throats facilitating exchange, flow channels and stagnant zones. Similarly, a tissue matrix might reduce to intra/extracellular spaces, flowing vascular/tubular spaces, macromolecular superstructure and possibly infiltrating malignant cells. The same »MR toolbox« (relaxation, diffusion/flow, internal gradients, chemical shift) is employed to disentangle these constituents and guide decision making, and the more complex the encoding pattern, the higher the power of differentiation. Efficiency is also important both industrially and clinically, and many applications call for the minimum sampling retaining the desired contrast. This tutorial will review examples where porous media techniques (particularly involving diffusion-weighted imaging (DWI)) are applied to physiological pathologies.

Tissue microstructure is one area with great overlap with porous media science. Diffusion-weighting in neurological tissue (neuronal networks in gray matter, or axonal nerve fiber bundles in white matter) has motivated many models with explicit physical dimensions, statistical parameters, empirical descriptors, or hybrids thereof. Diffusion anisotropy is particularly useful in schemes estimating nerve fiber connectivity. Double diffusion encoding techniques - which have origins in porous media science - have received significant attention for estimating cell size and/or eccentricity. Trabecular bone in skeletal joints is a porous network filled with a fluid/fat marrow mixture important in determining fracture risk. Trabecular structure may be directly resolved by microimaging, or inferred via susceptibility gradients, relaxation, or diffusion responses. Another effect with great clinical relevance is active flow. Kidney tissue shows significant active water transport (vascular/tubular flow) that manifests as »pseudodiffusion«, allowing DWI to probe filtration efficiency. Certain pathologies such as cancer involve anomalies in both structure and flow that MR tools can differentiate: hypervascularity increases the abundance of fast pseudodiffusion, while aggressive cellularity restricts passive diffusion. The tools of magnetic resonance and their interpretation in porous media has had great impact on their use in clinical MRI, and continued cross-fertilization of ideas can only enhance the progress of both fields.

[1] P.J. Basser, Proc. MRPM9, 2008, p.26-28.
[2] F.W. Wehrli, Proc., MRPM9, 2008, I-11.

2 Plenary

I1 **2D NMR Studies of Local Order, Disorder, and Dynamics in Zeolites and Layered Silicates**

Brad Chmelka[1], Sylvian Cadars[1,2,4], Darren Brouwer[3], Ramzy Shayib[1], Ming-Feng Hsieh[1], Lyndon Emsley[4], Dominique Massiot[2]
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Solid porous silicates often exhibit subtle combinations of short- and long-range structural order and disorder, as manifested by solid-state 1D and 2D ^{29}Si NMR and X-ray scattering measurements. Such features generally arise in the presence of organic structure-directing species that strongly interact with and direct the formation of co-assembling and/or co-crystallizing silicate networks, whose resulting structures are often difficult to establish. Heteronuclear ^{29}Si{^{1}H} dipole-dipole couplings allow interactions between the organic structure-directing species and silicate framework moieties to be measured and their interrelationships determined. Furthermore, homonuclear ^{29}Si{^{29}Si} scalar and dipole-dipole interactions can be used to establish the interconnectivities and local bonding environments among different sites in ordered silicate frameworks [1-4]. In combination with X-ray scattering and molecular modeling analyses, these yield new insights on the processes by which complicated silicate frameworks become ordered and provide important constraints that can be used to assess their local structures. Recent results will be presented that demonstrate the challenges involved and new opportunities available for understanding and establishing the structures of siliceous zeolites and layered silicates, including those for which scattering analyses are indeterminate.

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[2] S. Cadars, A. Lesage, N. Hedin, B.F. Chmelka, L. Emsley, J. Phys. Chem. B, 110, 16982-16991 (2006).
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$\boxed{\text{I2}}$ Restricted Diffusion of Hyperpolarized Helium-3 to Probe Lung Structure

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[1] Washington University

Hyperpolarized helium-3 offers a hgih spin sensitivity, allowing the air spaces of human and animal lungs to be imaged. Our group's focus has been on diffusion MRI of the lungs, probing structural features (e.g., airway and alveolar walls) that are too small to be imaged directly. In short-range ADC measurements, the diffusion time is typically 2 ms and the gas explores regions as large as 1 mm. Thus the acinar airways, with typical radii of 0.35 mm, substantially restrict the diffusion. An early successful application has been to distinguish healthy and emphysematous lungs (and regions within lungs) by their ADC. In health, the ADC is about 0.2 cm^2/s, compared to a free gas diffusivity of 0.88 cm^2/s. In emphysema, a disease characterized by airway expansion and airway/alveolar wall destruction, the ADC climbs by as much as a factor of 3, an unambiguous discrimination between healthy and diseased lung.

The signal decay from diffusion is fundamentally inhomogeneous in lung. There are airways oriented at essentially all orientations with respect to any gradient axis, and the diffusion along the airway (D_L) is much larger than the diffusion across the airway (D_T). The non-exponential signal decay measured with several values of diffusion-weighting b can be fit to determine the separate values of D_L and D_T. In turn, D_T can be used to establish the mean acinar airway radius R; the value of D_L determines the depth h that the alveoli penetrate into the airway channels. This is remarkably detailed information from a non-invasive measurement. Thus it has been named »helium-3 MRI lung morphometry«, a reference to the method it replaces: microscope examination of excised tissue.

Long-range ADC probes the motion of gas atoms over seconds and several centimeters. It uses spatial modulation of the longitudinal spin magnetization (SPAMM), or »striping«. Once the stripes are applied, the stripe amplitude decays and can be followed by repeated small-angle MR imaging. Long-range ADC is exquistely sensitive to collateral ventilation paths, small homes in airway walls connecting one airway to its neighbor. Not surprisingly, long-range ADC is even more sensitive to emphysema than is short-range ADC. Even in normal lungs, the long-range ADC is determined primarily by collateral paths. We have computer-simulated diffusion on the airway network and find it is much too slow to explain the measured long-range ADC in normal lungs. Instead, the important paths are collaterals, as confirmed by comparing long-range ADC in species with collateral paths (man, dog) and without (pig, sheep).

$\boxed{\text{I3}}$ Signals in Post-War Ruins, Five Orders of Magnitude and Pore Spaces Explored by Diffusion Measurement

Jörg Kärger [1]

[1] University of Leipzig

The presentation strives to justify Richard Ernst's appraisal of Leipzig as the "East Pole of Magnetic Resonance". Exploiting the special conditions of an after-dinner talk, the development of Magnetic Resonance in Leipzig is correlated with its history and its international rank as a city of sciences and arts. Molecular diffusion is selected as an example for illustrating the surprises which may be generated by scientific progress. This is in particular true for diffusion in pore spaces. Diffusion studies were recognized to provide an important novel route for the structural characterization of porous materials, including a detailed monitoring of the dynamic features of the guest species accommodated by these materials. Important features of great technological relevance, which otherwise would have remained unrecognized, have thus become accessible by direct measurement. Manifold activities in the field promise a most prosperous continuation of this development into future.

3 Invited Talks

I4 **Relaxation Analysis of Porous Media at High Magnetic Field Strengths: the Influence of Internal Gradients**

Jonathan Mitchell[1], *Thusara Chandrasekera*[1], *Tegan Roberts*[1], *Edmund Fordham*[2], *Lynn Gladden*[1]

[1] University of Cambridge, [2] Schlumberger Cambridge Research

It is well known that internal magnetic field gradients, caused by susceptibility differences at solid-liquid interfaces, alter transverse relaxation times observed in liquid-saturated porous media. As such, CPMG measurements provide only an effective $T_{2,\text{eff}}$ relaxation time determined by molecular diffusion, rather than the true T_2 relaxation time determined by solid-liquid interactions. In order to overcome the influence of internal gradients, NMR data can be acquired at low magnet field strengths. Of course, the definition of low field needs to be quantified in order to optimise experimental parameters, and a simple calculation for estimating the maximum magnetic field strength is presented. However, the use of low magnetic fields is not a universal solution: this can be disadvantageous in some circumstances, where suitable magnets are unavailable, or if chemical sensitivity is required. It is known that internal gradients increase with magnetic field strength, and so it is important to understand the role of these gradients in high field NMR measurements.

The strength of the internal gradients will determine the diffusion behaviour observed, and three significant diffusion regimes need to be considered when measuring $T_{2,\text{eff}}$ relaxation times in porous media: the motional averaging regime is governed by pore size; the short time regime is governed by the CPMG echo spacing; and the pre-asymptotic localization regime is governed by the magnetic field profile in individual pores. By measuring $T_{2,\text{eff}}$ across a range of magnetic field strengths, it is possible to observe the diffusion behaviour in different regimes. Here, we demonstrate techniques for examining distributions of effective internal gradient g_{eff} and diffusion behaviour. For example, it is possible to observe exchange between regions of different gradient strength using two-dimensional T_2–T_2 measurements. This method is demonstrated in brine saturated reservoir rock plugs.

It is also possible to deconvolve the contributions from diffusion and surface relaxation, allowing the true T_2 relaxation time to be obtained from measurements of $T_{2,\text{eff}}$ acquired in the presence of internal gradients. This is of importance when measuring the ratio T_1/T_2 as a function of magnetic field strength in order to determine surface mobility of adsorbed species. According to theoretical predictions, both T_1 and T_2 relaxation times should increase with magnetic field

strength; this is observed for T_1 but not $T_{2,\text{eff}}$. However, the true T_2 relaxation time does indeed increase, as demonstrated in packed beds of glass spheres. As such, correct T_1/T_2 ratios can be obtained even using high field spectrometers that would have been deemed inappropriate previously for the study of liquid-saturated porous media. The determination of corrected T_2 relaxation time distributions are discussed in the light of results from heterogeneous catalyst supports.

I5 The Use of Internal Magnetic Field to Characterize Porous Media

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[1] Schlumberger-Doll Research

When a porous material is placed inside a magnet, the magnetic field inside the pore space is naturally inhomogeneous due to the susceptibility contrast. Such internal field is ubiquitous in materials and intimately related to the packing structure of the grains and can be used as a fingerprint of the material. This talk will outline several magnetic resonance imaging (NMR and MRI) techniques, the underlying diffusion physics to quantify the internal field, spatial correlation, and their application in the study of pore structure of rocks and biological tissues.

I6 Intracellular Confinement of Magnetic Nanoparticles by Living Cells: Impact for Imaging and Therapeutic Applications

Florence Gazeau[1]
[1] Lab MSC, CNRS/Université Paris Diderot

Magnetic labelling of living cells creates opportunities for numerous imaging and therapeutic applications such as cell manipulation, magnetically-induced hyperthermia or MRI cell tracking. The unique advantage of magnetic-based methods is to activate or monitor cell behavior by a remote stimulus, namely the magnetic field. Cell labelling methods using superparamagnetic nanoparticles have been developed, showing no adverse effect on cell proliferation and functionalities, while conferring magnetic properties to various cell types. Magnetic nanoparticles are internalized by living cells within intracellular compartments, which confine the nanoparticles at high concentration.

The ability of iron oxide nanoparticles to create MRI contrast or to generate heat under alternating field is governed by the dynamical behavior of their magnetic moment. The dynamics results both from Brownian motion of the particles and from internal fluctuations of the magnetic moment within the nanocristal (N?el dynamics). Intrinsic properties of nanoparticles, such as their size, their magnetization and their magnetic anisotropy, are the relevant parameters governing the dynamics. However environmental characteristics such as the local viscosity or the way nanoparticles are organized within intracellular compartments, also affect their behavior.

We will present the effect of cellular environment on nanoparticle properties, stressing the role of interparticles magnetic interactions created by intracellular confinement.

Intracellular confinement will be shown to influence the MRI contrast properties of nanoparticles, their detectability as well as their efficiency as heating mediators.

I7 Magnetic Resonance Imaging for Petroleum Reservoir Core Analysis

Bruce Balcom[1]
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Despite laudable efforts to diversify the world energy supply, the industrialized world will remain dependent on petroleum for economic development and prosperity for many decades. Despite the importance of petroleum resources however, typical reservoir recovery rates are often no better than 40 %. Increasing these recovery rates requires detailed scientific knowledge of the fluid behavior in reservoir rocks. In addition, new reservoir exploration and development around the world is increasingly occurring in marginal reservoirs where the fluid or rock matrix properties are challenging, or in inhospitable environments such as the far north or offshore. In each case detailed knowledge of the fluid and matrix properties aid decision-making such as how to develop the reservoir, or indeed whether the reservoir is economic to develop at all.

In each of the two cases outlined above magnetic resonance imaging is able to decisively contribute to improved scientific knowledge of the fluid and matrix properties. MRI has the unique ability to analytically determine fluid content non-invasively as functions of space and time. MRI methods for core analysis include SPRITE fluid density imaging and new T_2 mapping spin echo methods. The use of these methods for laboratory core analysis and evaluation of enhanced oil recovery strategies will be described.

I8 Phase State and Dynamics of Fluids in Mesoporous Solids

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Mesoporous solids represent an important class of materials widely used in different applications in various fields including chemical engineering, material science and pharmaceutics. In particular, mesoporous hosts attract special attention due to their fascinating match of transport, geometrical and chemical properties [1]. By tailoring pore structure in these materials, their properties may be efficiently tuned to meet specific application-oriented purposes. Therefore, fundamental understanding of the correlations between the geometrical features of mesoporous solids, the phase state of confined therein fluids and their transport properties is an important factor for routing synthesis of novel

host systems and their optimal use in practical applications.

In this contribution, recent advances related to establishing of such interrelations in mesoporous materials using nuclear magnetic resonance will be reviewed. Among different topics, diffusion behavior of fluids during gas-liquid [2], solid-liquid [3] transitions, transition to the supercritical state [4] and kinetic effects accompanying hysteretic phase transitions in disordered matrices [5-6] will be discussed. In particular, it will be shown that molecular diffusivity may serve as a sensitive microscopic parameter of the system thermodynamic state.

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[3] Dvoyashkin, M., Khokhlov, A., Valiullin, R., and Kärger, J.: Freezing of fluids in disordered mesopores, J. Chem. Phys., 129 (2008) 154702.

[4] Dvoyashkin, M., Valiullin, R., Kärger, J., Einicke, W.-D., and Gläser, R.: Direct assessment of transport properties of supercritical fluids confined to nanopores, J. Am. Chem. Soc., 129 (2007) 10344.

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[6] Kondrashova, D., Reichenbach, C., and Valiullin, R.: Probing pore connectivity in random porous materials by scanning freezing and melting experiments, Langmuir, 26 (2010) 6380.

$\boxed{\text{I9}}$ Experience of Large-Scale NMR Measurements in Porous Media

Anatoly Legchenko[1], *Jena-Michel Vouillamoz*[1]
[1] Institute de Recherché pour le Développement (IRD) - LTHE

The proton Magnetic Resonance Sounding (MRS) is a geophysical technique that allows non-invasive investigations of water-saturated rocks. The method is based on the Nuclear Magnetic Resonance (NMR) phenomenon in the Earth's magnetic field. The measuring setup consists of a wire loop on the surface that is energized by one or two pulses of oscillating current. The frequency of the current is set equal to the Larmor frequency in the geomagnetic field that varies between 800 and 2800 Hz around the world. After the pulse is cut off, the free induction decay (FID) and/or the spin echo (SE) signals from groundwater could be measured. MRS results are averaged over the investigated volume that depends on the loop size and typically varies from $20 \times 20 \times 20$ to $100 \times 100 \times 100 \, \text{m}^3$.

MRS performance depends on the magnitude of the natural geomagnetic field, the electrical conductivity of rocks, the electromagnetic noise and other factors. For example, the maximum depth of groundwater detection for currently avail-

able equipment can vary from 45 to 170 m depending on measurement conditions, although an average depth of investigation is generally considered to be about 100 m.

Our recent results show that combination of FID and SE allows rendering the MRS less dependent on the geological conditions. Because of different scales, use of rock samples for calibration of the MRS estimate of the water content is difficult or impossible. Thus, for interpretation of experimental data we use a mathematical model that allows computing the theoretical signal generated by groundwater. The processing of MRS data can provide the depth, thickness and water content of investigated aquifers. The existing models are simplified and real experimental conditions of the MRS experiment may not obey the approximations that were made in the mathematical models and MRS is not always able to provide robust estimates of the MRS water content. For improving estimate MRS results we use calibration based on borehole pumping test data. Based on the water content and the relaxation time provided by MRS it is possible to estimate the aquifer's hydrodynamic properties. In this aim, experience gained through NMR logging has been applied to MRS data interpretation. Presented discussion of the advantages and disadvantages of the MRS, the accuracy of the MRS results and of the practical limitations of the method allows better understanding of this geophysical technique.

I10 Halbach Arrays for NMR and MRI

Juan Perlo [1], *Ernesto Danieli* [2], *Bernhard Blümich* [3], *Federico Casanova* [4]
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During the last decade several magnet designs based on a Halbach arrays has been proposed for desktop NMR instruments. Compared to conventional C-shaped magnets, Halbach arrays accommodate larger samples inside the magnet bore and thanks to their jokeless design they are relatively small and light. In theory, the magnetic field generated by an infinitely long cylindrical Halbach array is perfectly uniform over the whole magnet bore. However, due to variations of the polarization of the magnet pieces used in the assembly, the magnetic field found in real magnets is strongly inhomogeneous. The field variation is such that only a small fraction of the bore can be excited. This is the reason why previously published magnets have been used for relaxation measurements while MRI and high-resolution spectroscopy are excluded. To cope with this problem, Halbach magnets have been scaled up, or the samples simply reduced, but then Halbach arrays became in practice as bulky and heavy as state of the art C-shaped magnets. Further drawbacks of the Halbach design are the complexity of the design and its associated manufacturing cost and the impossibility of placing high permeability materials, like iron pole shoes, in the inner bore of the magnet. Pole shoes smooth out the fast spatial variations of the magnetic field due to the local inhomogeneity of the magnet pieces leaving

mostly first and second order terms what can efficiently be corrected by simple electrical shim coils.

We have recently presented a robust method for correcting strong field inhomogeneities of the order of several thousands of ppm like the ones found in the stray field of single-sided magnets. The method is based on the displacement of magnet pieces specially designed in order to allow the generation of field variations orthogonal in space such as the spherical harmonics. The first implementation of the method was to generate a spot of highly homogeneous field (fraction of ppm) outside the magnet for single-sided ^{1}H spectroscop. Later, the method was extended to correct the field inhomogeneities of a Halbach magnet for MRI. In that case, a second Halbach array made of movable pieces was placed in the bore of an existing Halbach to efficiently generate first and second order shim terms. Finally, the method was refined by incorporating the movable pieces into the main magnet design and extending the correcting shim terms to higher orders [1]. Here we present the implementation of this approach to design and build Halbach magnets generating homogenous field for the several proposes, like, for example, miniature magnets for high-resolution spectroscopy, low field/low weight magnets for T_2 relaxometry of large samples, and desktop MRI systems.

[1] E. Danieli, et al., Small Magnets for Portable NMR Spectrometers. Angewandte Chemie International Edition. 49 (2010) p. 4133-4135.

$\boxed{\text{I11}}$ **Application of Hyperpolarized Xenon-129 NMR to Single File Diffusion and Exchange Dynamics in Nanoporous Materials**

Clifford Bowers[1], *Chi-Yuan Cheng*[1], *Theocharis C. Stamatatos*[1], *George Christou*[1]
[1] University of Florida

Supramolecular materials often exhibit porosity over a wide range of length scales and with diverse pore space architectures. Particularly intriguing are crystalline solids exhibiting one-dimensional pores, which afford a high adsorption capacity with size selectivity and uni-dimensional diffusion properties. For basic studies of molecular diffusion in one-dimension, the material should have well-defined, defect-free channels with tuneable and monodisperse diameters. Here, hyperpolarized xenon-129 NMR techniques are presented for studying diffusion and Xe exchange in nanotubes formed by molecular wheel compounds. A large family of molecular wheels has been reported in the literature over the past two decades, typically with a single-strand topology with respect to the metal ions. Particularly beneficial synthetically has been the use of a central template whose size and nature determine the size (metal nuclearity) of the resulting wheel that forms around it. However, such central templates prevent the crystal from exhibiting nanoporosity. In contrast, recent work replacing the MeO$^-$ groups of Fe$_{10}$(OMe)$_{20}$(O$_2$CMe)$_{10}$, and the corresponding Ga$_{10}$(OMe)$_{20}$(O$_2$CMe)$_{10}$ (abbreviated Ga$_{10}$) analogue, with 1,3-propanediolate

(pd^{2-}) has provided a non-template means to change the wheel size, as in [M$_{18}$(pd)$_{12}$(pdH)$_{12}$(O$_2$CMe)$_6$(NO$_3$)$_6$](NO $_3$)$_6$ (M$_{18}$; M = Fe or Ga) [1]. In fact, both the M$_{10}$ and M$_{18}$ wheels have empty central cavities, and in the crystal they thus stack to form supramolecular nanotubular channels of monodisperse diameters. This talk will focus on the application and development of hyperpolarized ^{129}Xe NMR [2-5] methods to study diffusive transport and gas exchange in molecular wheel nanotubes of different channel sizes. The availability of two different wheel sizes provides the opportunity to study unidirectional diffusion as a function of the central cavity diameter. Evidence of single file diffusion of Xe atoms in the Ga$_{10}$ crystals is consistent with the relative size of the Xe atom with respect to the channel diameter. Furthermore, the diffusion of gas atoms between the nanochannels and the bulk gas phase was observed by continuous and interrupted-flow hyperpolarized ^{129}Xe 2D exchange NMR. The results presented here illustrate how hyperpolarized NMR can characterize molecular transport in materials with one-dimensional pore structures.

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[4] Cheng, C.-Y.; Bowers, C. R. ChemPhyschem 2007, 8, 5.
[5] Cheng, C. Y.; Bowers, C. R. Journal of the American Chemical Society 2007, 129, 13997-14002.

I12 Pulmonary Physiology with Hyperpolarized ^{129}Xe

Samuel Patz[1], *Iga Muradyan*[2], *Mirko I. Hrovat*[3], *James P. Butler*[4]
[1] Harvard Medical School, [2] Brigham and Women's Hospital, [3] Mirtech, Inc., [4] Harvard School of Public Health

The purpose of the lung is gas exchange; O_2 diffuses from alveolar gas spaces to blood and CO_2 diffuses in the reverse direction. Efficient gas exchange occurs because of the large alveolar surface area ($\sim 100\,\mathrm{m}^2$) and thin tissue barrier ($< 1\,\mu\mathrm{m}$) separating alveolar gas and capillary blood. Reduction of surface area or thickening of the tissue barrier layer reduce the diffusing capacity of the lung. To diagnose and determination of treatment efficacy in pulmonary disease, methods are needed to noninvasively measure sub-components of lung physiology. To that end, we describe here a magnetic resonance method to evaluate three parameters: alveolar surface area per unit volume (S/V) which decreases in emphysematous disease; septal thickness, which increases in interstitial disease; and capillary transit time, which is a function of pulmonary hypertension and vascular health.

Because of a large chemical shift between ^{129}Xe in gas and tissue/blood, it is straightforward to measure the septal uptake of ^{129}Xe in tissue and blood (dis-

solved phase). After selective saturation of the dissolved phase magnetization (M_{Xe}), we observe the recovery of M_{Xe}. We call this method Chemical Shift Saturation Recovery (CSSR). Initially, M_{Xe} increases diffusively as $\sqrt{t}$ with a proportionality constant of S/V [1]. After ~ 100 ms, the septa begin to saturate with ^{129}Xe and the time dependence of the xenon septal uptake begins to level off to a plateau, the value of which is proportional to the septal thickness. Because of blood flow, however, M_{Xe} does not plateau and continues to increase at long times. Fits of human xenon septal uptake curves to a 1D analytical model of this process provides estimates of S/V, septal thickness and capillary transit time [2].

We obtained whole lung results using the CSSR method in 4 healthy subjects, 2 subjects with mild to moderate COPD, and 2 subjects with mild to moderate interstitial lung disease (ILD). The COPD subjects showed a remarkable reduction (more than a factor of 4) in S/V compared to the normal subjects whereas the two ILD subjects showed an increase in septal thickness compared to our normals of 36 and 97 %.

More recent experiments were performed with a modified version of the Xenon Transfer Contrast (XTC) method [3] to obtain 3D regional maps of S/V in a healthy subject [4]. Rather than direct observation of dissolved phase ^{129}Xe magnetization in CSSR, XTC measures the reduction in the gas phase ^{129}Xe magnetization by allowing multiple opportunities for interphase diffusion. We have demonstrated that analytically identical results to CSSR can be obtained with XTC if π pulses are used for the gas exchange sensitization portion of the pulse sequence rather than the traditional $\frac{\pi}{2}$ pulses.

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[4] Patz et al., ISMRM 2010, Stockholm.

I13 Detecting Fleeting MRI Signals with Frequency-Modulated Radio Waves

Michael Garwood[1], Djaudat Idiyatullin, Curtis Corum, Steen Moeller, Ryan Chamberlain, Robert O'Connell, Naoharu Kobayashi
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A fundamentally different approach to MRI is described called SWIFT (sweep imaging with Fourier transformation) [1,2]. SWIFT exploits time-shared RF excitation and signal acquisition, allowing capture of signal from spins with extremely short transverse relaxation time, T_2^*. MR signal is acquired in gaps inserted in a broadband frequency-swept excitation pulse, which results in acquisition delays of only 1–2 microseconds. In SWIFT, 3D k-space is sampled in a radial manner, whereby one projection of the object is acquired in the gaps of each frequency-swept pulse, allowing a repetition time (TR) on the order of the

pulse length (typically 1–3 milliseconds). Thus, SWIFT images can be acquired in scan times similar to and sometimes faster than conventional 3D gradient echo techniques. Because the orientation of consecutive projections varies in a smooth manner (i.e., only small increments in the values of the x, y, z gradients occur from view to view), SWIFT scanning is close to inaudible and is insensitive to gradient timing errors and eddy currents. With its ability to capture signals from ultrashort T_2^* spins, SWIFT promises to expand the role of MRI in areas of research where MRI previously played no or negligible role. Broadband frequency-swept excitation and extremely short acquisition delay make it possible to preserve signals from spins experiencing large frequency shifts due to magnetic susceptibility effects. For example, superparamagnetic-labeled nanoparticles (e.g., SPIOs), which cause signal avoids in images acquired with a conventional gradient echo sequence, give rise to positive contrast (bright spots) in SWIFT images [3]. Early experience suggests SWIFT can play a role in materials science and porous media research. One conceivable advantage will be for capturing signals in heterogeneous porous media with strong surface relaxivities (e.g., due to abundant iron or manganese) [4].

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I14 Diffusion in White Matter

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Diffusion magnetic resonance imaging permits non-invasive probing of tissue microstructure and function and provides invaluable information in brain diagnostics. Conventional methods are based on a simplified picture of Gaussian diffusion of water molecules in brain tissue characteristic of the isotropic non-confined liquids. However, more detailed experiments show that water in brain tissue tends to exhibit essential deviations from patterns of the Gaussian diffusion. The propagation of water molecules in the brain and in biological tissue, in general, is affected by multiple factors such as compartmentalization, restric-

tions and anisotropy imposed by the cellular microstructure [1,2] which can be modelled, quite in general, as a composite porous medium [3,4]. Interfacial interactions with the cell membranes (»bound water«) and exchange tend to further complicate the measured response. Due to the heterogeneity and complexity of the tissue microstructure, a differentiation between the various contributions to the average NMR signal in in vivo studies represents a difficult task. Our aim is to develop the advanced approaches capable of capturing more detailed information on the propagation mechanisms and underlying tissue microstructure in comparison to conventional methods. In this work, we will present a diffusion study of the brain based on the detailed analysis of the attenuation patterns in the extended range of the diffusion-encoding gradients. Experimental data are based on the in vivo studies of healthy volunteers and on the measurements of artificially constructed anisotropic »phantoms«. The discussion will be supported by results of random-walk Monte Carlo simulations [5] in the well-defined model systems relevant for the structural organisation of white matter.

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I15 Linking Soil Science with NMR Relaxometry: Potential and New Challenges

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^{1}H-NMR-Relaxometry is being increasingly applied in soil science due to its potential for helping to understand water uptake into the soil matrix and processes occurring at the solid-liquid interface at soil particle surfaces. This contribution discusses current applications of proton NMR relaxometry in the context of soil science and identifies its potential and current research gaps. NMR relaxometry is a sensitive, informative and promising method to study pore size distribution in soils as well as many kinds of soil physicochemical processes, among which are wetting, swelling or changes in macromolecular status. It is further a very helpful method to study interactions between molecules in soil organic matter and can serve to study the state of binding of water or organic chemicals to soil organic matter. Relaxation times determined by NMR relaxometry are sensitive to various factors that play a role in soil-water interaction which is both an advantage and shortcoming of the method: NMR relaxometry can be applied to numerous investigations in soil science, but at the same time interpretation of the results is challenging in such complex and heterogeneous systems like soils.

I16 High-Throughput Low Resolution NMR Methods to Analysis of Agri-Food Products

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We have recently proposed a low resolution NMR method termed continuous wave-free precession (CWFP) to enhance signal-to-noise ratio in quantitative analysis, measuring flow, longitudinal (T_1) and transverse relaxation time (T_2) measurements in a single experiment, and thermal diffusivity measurements in a few seconds. We have been using this sequence for on-line and non-destructive measurements of agri-food products based on a low resolution NMR spectrometer. The on-line spectrometer is based on a CAT 100 NMR transceiver, Tecmag, a 30 cm bore, 2.1 T superconducting Oxford magnet and in a homemade polycarbonate conveyor belt, drived by a Parker step motor.

The CWFP regime is attained when a train of short pulses, with period Tp small as compared to T_2^* is applied to a liquid or heterogeneous sample. This causes the amplitude of the transverse magnetization just preceding pulse to be equal to the amplitude following the pulse. Since the condition $T_p < T_2^*$ implies that dephasing of isochromats in each interval Tp is relatively small, a continuous wave periodic signal with practically constant amplitude, displaying n nodes within each T_p interval, is obtained. Therefore, the CWFP signal can be observed continuously for arbitrary long periods of time while a stream of samples is conveyed to the NMR receive/transmit coil. The CWFP sequence has the potential to measure the oil content in more than 20.000 samples per hour or to measure the intramuscular fat content in more than 500 beef portions/hour.

Using the same on-line spectrometer and CPMG pulse sequence we have been measuring the oil quality in intact seeds. The CPMG decay processed by chemometric methods was able to determine the oil quality in intact seeds by its fatty composition, cetane number, iodine value and kinematic viscosity with a correlation coefficient $r > 0.9$. The automated NMR system has the potential to analyze more than 1000 samples per hour. The CPMG sequence has also been used to detected mechanical injuries in fruits such as banana, pears.

I17 Characterisation of Heterogeneous System by PFG-NMR

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In heterogeneous media, as food stuff or rock cores saturated with crude oil and/or brine, the use of pulsed field gradients is an essential for resolving the NMR response from the different components. In addition one may use the diffusion measurements themselves to extract information about the environment in which the diffusing molecules are confined.

Ever since Mitra et al. (Physical Review B 47 (1993)) introduced the short observation time expansion of the observed diffusion coefficient, resolving the

surface to volume ratio (S/V) from the surface relaxivity (ρ) we have focused on developing applications where this model has been used. This short observation time model is unique as it resolves the surface to volume ratio from the surface relaxivity, and thus makes it possible to either measure the S/V directly or combine it with relaxation time measurements to extract pore size distributions in rock core plugs or droplet size distributions in emulsions.

In our work with developing methods for characterising emulsions, a major obstacle has been the settling time for the system to regain the thermal equilibrium along the external magnetic field (~ 5 times T_1) between each scan. Instead of letting the magnetisation reach thermal equilibrium before each scan, we apply a combination of RF-pulses and magnetic field gradients which aim at spoiling any magnetisation in any direction. Then, using a waiting time equal to T_1 after the spoiling, we have already regained 63% of the magnetisation at thermal equilibrium. The waiting time between each scan is then reduced to practically nothing, and the total experimental time may be reduced by as much as 80% without any significant loss of signal to noise. As a consequence we may use the spoiler approach to reduce the acquisition time of two dimensional experiments, as Diffusion-T_2 or T_1–T_2, from the order of hours to the order of minutes.

The acquisition time is an important issue when you for example are to analyse biological tissue, a biopsy, during surgery. By using the spoiler approach we reveal information that may assist the surgeon to decide the best approach for the surgery of a patient.

4 Oral Contributions

4.1 Connected Porous Systems and Multidimensional NMR Approaches

O1 Propagator-Resolved 2D Exchange in Porous Media in the Inhomogeneous Magnetic Field

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We present a propagator-resolved 2D exchange spectroscopy technique for observing fluid motion in a porous medium. The susceptibility difference between the matrix and the fluid is exploited to produce an inhomogeneous internal magnetic field, causing the Larmor frequency to change as molecules migrate. We test our method using a randomly packed monodisperse 100 micron diameter glass bead matrix saturated with distilled water. Building upon previous 2D exchange spectroscopy work we add a displacement dimension which allows us to obtain 2D exchange spectra that are defined by both mixing time and spatial displacement rather than by mixing time alone. We also simulate our system using a Monte Carlo process in a random nonpenetrating monodisperse bead pack, finding good agreement with experiment. A simple analytic model is used to interpret the NMR data in terms of a characteristic length scale over which molecules must diffuse to sample the inhomogeneous field distribution.

O2 Determination of Surface Relaxivity and Fluid Configuration in Fluid Saturated Porous Media

Martin Hurlimann[1], *Lukasz Zielinski*[1], *Andre Souza*[2]
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The extraction of pore size distributions from relaxation measurements in fluid saturated porous media requires a value of the surface relaxivity ρ, a property that characterizes the efficiency of surfaces to relax spins. With the knowledge of ρ, the measured relaxation times can then be directly related to geometrical length scales of the pore space. Here we demonstrate that the surface relaxivity can be obtained self-consistently with NMR measurements that can be performed ex-situ. This eliminates the need for external pore size calibration. The approach is based on 2d diffusion-relaxation experiments and takes advantage of the fact that molecular collisions of the saturating fluid with the solid surfaces

that cause surface relaxation also hinder the diffusion of the molecules, reducing their mean squared displacement. By monitoring the degree of restriction for spins with a given relaxation time T_2, the surface relaxivity can be directly determined. In pores that are large compared to the diffusion length L_D, the reduction of the mean squared displacement relative to the unrestricted case is proportional to $L_D/(\rho T_2)$. By plotting the mean squared displacement for different T_2 components versus the relaxation rate $1/T_2$, it is possible to extract ρ from the initial slope. This parameter is not only a calibration parameter that relates relaxation time with geometrical length scales, but gives information about the surface properties, including mineralogy, surface roughness and concentration of paramagnetic impurities. Repeating the measurement with different values of diffusion lengths, we have confirmed that the scaling of the mean squared displacement with L_D/T_2 is consistent with the hypothesis of uniform ρ throughout the pore space. We have observed that this scaling often holds beyond the range where L_D/T_2 is small. This indicates that the connectivity of the pore space at different length scales is similar, at least over the dynamic range that can be probed with the current experiments.

Furthermore, when the samples are saturated with two immiscible fluids, this analysis gives information about the fluid configuration within the pore space. In mixed-saturated porous media, molecules encounter additional interfaces at the boundaries separating the different fluids. These fluid-fluid interfaces, while typically only weakly-relaxing, still restrict the motion of the spins. The effective surface relaxivity for a given fluid extracted from the diffusion-relaxation analysis in such samples is then reduced by the ratio of the total surface of that fluid to the surface of the interface between that fluid and the solid matrix. This ratio is determined by the fluid configuration within the pore space, which in turn is controlled by the wettability of the rock. For oil reservoir rock, wettability is of paramount importance as it determines the optimal strategy to attain the best oil recovery rate.

O3 Multidimensional Rotating Frame Correlation of Relaxation Dispersion

Ravinath Kausik[1], Lukasz Zielinski[1], Martin Hurlimann[1]
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We present the novel technique of multidimensional rotating frame correlation of relaxation dispersion (RFCORD) to probe low frequency dynamics of complex fluid systems. By mapping out correlations in the spectral density at selected frequencies in the window of $500\,\text{Hz}$ to $100\,\text{kHz}$, RFCORD is sensitive to the range of correlation times of particular interest in the study of exchange and aggregation processes in colloidal systems or fluid-saturated porous media. Such systems are often heterogeneous and typically contain multiple components with different dynamics. The RFCORD pulse sequence consists of an initial hard 90°_x pulse followed by a spin locking pulse of amplitude w_{1A} for duration t_A, imme-

diately followed by a second spin-locking pulse of amplitude w_{1B} of duration t_B. The intervals t_A and t_B are varied systematically to cover the whole range of $T_{1\rho}$ values in the system. The correlation distribution between $T_{1\rho}$ corresponding to w_{1A} and w_{1B} is obtained by a two-dimensional inverse Laplace transformation with respect to t_A and t_B.

Cheese is a common heterogeneous water-fat complex, where each phase has not only different relaxation times but also very different dynamics, as the fat is in the extreme narrowing regime and the water undergoes exchange with casein micelles. Using RFCORD we show how the correlations between 9 kHz and 1.5 kHz, directly demonstrate these features. The signal corresponding to the motionally averaged fat components is clearly shown to lie on the diagonal, whereas the water signal is shifted off the diagonal. This indicates that the water molecules are involved in slow exchange and that the corresponding spectral density varies in the selected frequency interval. Varying the strength of the rotating field with the effect of scanning the frequency, results in the shifting of the water peak only, as the dispersion of the fat in this case is flat.

This technique also opens up the unique possibility of being combined with standard spectroscopy to yield chemical shift resolved correlation of relaxation distributions, thus adding a Fourier dimension to the analysis. The standard T_1–T_2 or T_2–T_2 correlation spectroscopy is most sensitive to correlation times near the Larmor frequency and does not have the ability to vary the measurement frequency. While field-cycling has this ability, it is limited at low-frequencies by ~ 10 kHz and also requires expensive specialized hardware. On the other hand, therotating field relaxation has the potential of universal application on standard superconducting and mobile systems and even *ex situ* measurements.

O4 Using Multi-Frequency NMR Relaxation for Probing Wettability in Multimodal Porous Rocks

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We present a new method for probing wettability of rock/oil/brine systems using nuclear magnetic relaxation dispersion (NMRD) [1]. This technique measures the variation of proton spin-lattice relaxation rates $1/T_1$ as a function of magnetic field strength or nuclear Larmor frequency. Unlike conventional transverse relaxation studies, this approach gives a direct probe of the dynamical surface affinity of fluids, thus allowing the separation of wetting from non-wetting fluids through their typical NMRD features. To quantify these features we introduce a microscopic dynamical surface affinity index which measures the dynamical correlation (i.e. microscopic wettability) between a diffusive fluid and fixed paramagnetic relaxation sources at the pore surfaces. For the first time we apply this technique to carbonate reservoir rocks of bimodal porosity saturated with oil ($S_w = 0\,\%$), brine ($S_w = 100\,\%$) and mixture of oil/brine ($S_{w,irr}$).

The measured NMRD features clearly discriminate the wetting behavior of the fluids in the pore system. We have interpreted these different NMRD profiles in a model of dynamical surface relaxation. We consider two different situations for the proton exchange properties:

(i) for an aprotic liquid such as oil (dodecane), the affinity index varies between 1 (bulk i.e. non wetting case) and infinity (strong surface affinity i.e. wetting case). This index quantifies the degree of dynamical correlation with the paramagnetic impurities present at the pore surface.

(ii) for a protic liquid such as brine, we define a similar index by comparing the time of residence of a proton in the ligand field of the paramagnetic ions to the electronic spin-lattice relaxation time (i.e. reflecting the presence of water close to the surface and thus a water-wetting behaviour). The experimental results obtained on carbonate core plugs of bimodal porosity saturated with an oil/brine mixture ($S_{w,irr}$) have been processed using the proposed model and clearly reveal the pore size dependence of wettability.

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O5 NMR Relaxometry of Cement Pastes

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Concrete is an inherently low energy input material (600–800 MJ/tonne) comparable to wood (500 MJ/tonne). However, the enormous quantities used worldwide mean that it accounts for at least 5 % of global CO_2 production with demand for cement set to at least double by 2050. Water movement in concrete is key factor influencing the long term performance and degradation of infrastructure by both physical and chemical means. Water is a key constituent of cement, the primary binder phase of concrete. As yet there is no clear understanding of pore-water interactions in cements. This understanding is required to enable confidence in the use of new, more environmentally friendly, cement based materials. Nano-scale pores in cement are essentially planar. In a recent study we have shown how the ratio of the longer component of the FID/CPMG signal amplitude compared to the solid echo signal amplitude as a function of sample water content can be used to provide an estimate the width and relative specific area of the intra C-S-H sheet pores between the tetrahedral silica sheets of C-S-H and of the inter C-S-H particle gel pores. The measurement is based on the observation that as water is removed, so the surface fraction contributing to the solid echo increases. Account is taken of carbonation effects. The new results are in broad agreement with previous estimates from more usual NMR analyses based on the relaxation times. However, the method used has the advantage that it is not necessary to calibrate the surface relaxivity. A further parameter of interest is the lateral extent of the pores. We suggest how observation of double quantum filtered signals in grey cement with Fe^{3+} impurities offers a possible entry to measuring this. Taken altogether, the measurements are

providing estimates of the typical size of the nano-scale calcium silicate hydrate structures that together make up cement gel.

O6 Spatially Varying Surface-Relaxivity and Diffusion-Controlled Magnetic Relaxation in Complex Porous Media

Seungoh Ryu[1], Gabriela Leu[1], David Linton Johnson[1]
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The diffusion/relaxation behavior of the magnetization reflects the underlying geometry and the composition of filling fluids in a variety of porous media. For example, the magnetic resonance (MR) probes are used for the key transport and fluid compositional properties of the formation in the oil industry. As the importance of reservoirs with complex pore geometry grows, however, limitations imposed by simplifying assumptions become more pronounced.

A key issue is regarding how robust the mapping is between the relaxation spectra and the pore geometry when the latter becomes extended and heterogeneous. In such cases, the conditions which warrant the simple mapping break down, and there is growing need to quantify the degree to which the shortcomings impact the interpretation of empirical data such as the 2D-NMR relaxometry in real rocks. This is further complicated by the potential effect of spatially varying surface-relaxation strength, $\rho(r)$, which may compete with the purely geometrical aspects of the issue in obscuring the mapping [1].

We recently developed an efficient numerical modeling method that enables simulations of relevant MR processes on 3D pore space based on the high resolution micro-tomography of rock cores. Laboratory measurements are made on the same rock for direct comparison. Through a series of simulations with controlled model-parameter (such as $\rho(r)$, temperature, etc) variations, we determine unambiguously whether the system is in the diffusion-controlled or surface-relaxation controlled regime. We find some evidence that NMR response is diffusion-controlled in certain rocks we investigated this way. We also address the issue of spatial variation in rho for realistic cases. Through analytic solutions and numerical simulations, we determine the bounds on its impact on the interpretation of surface-induced relaxation spectra [2].

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4.2 Micro- and Nanostructured Materials

O7 **MRI and PGSE NMR Studies of Long-Range Pore-Pore Interaction Effects in Gas Adsorption**
Iain Hitchcock[1], Sean Rigby[1], John Chudek[2], Liz Holt[3], John Lowe[1]
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It has been demonstrated using optical imaging methods that pore-blocking can give rise to sample-spanning clusters of pores filled with meta-stable adsorbate on the desorption branch of isotherms. However, long-range, pore-pore interactions on the adsorption branch are rather less well studied. Pore-pore interaction effects during adsorption, such as advanced condensation, have been proposed, but only studied using one-dimensional, non-spatially resolved techniques, such as sorption scanning loops.

In this work magnetic resonance imaging (MRI) methods will be used to study long-range effects during adsorption of water within a model mesoporous silica material. Previous studies of fully-saturated samples have suggested that the void space of the model material possesses macroscopic length-scale ($\sim 300\,\mathrm{mm}$) correlations in the spatial distribution of pore sizes, such that the pore size distribution can be imaged directly using MRI. Hence, the model material can be used to directly study interactions between neighbouring void space regions with different pore sizes.

Spin-spin relaxation time (T_2) contrasted images have been obtained at different relative pressures during adsorption of water onto the model material, as previously proposed. Analysis of the variation in spin density (proportional to amount adsorbed) and T_2 (proportional to the characteristic size of condensed phase) in the voxels across the image have enabled a determination of the mechanism of adsorption within this material. It was observed that, at each relative pressure, there were roughly normal-shaped distributions in spin density and T_2, where the mean of the distributions steadily increased with relative pressure. This pattern of results is more consistent with a continuous pore-filling mechanism, rather than multi-layer build-up followed by abrupt capillary condensation (where bi-modal distributions might be anticipated).

In addition, the reduced widths of the distributions in T_2 were wider for partially saturated samples, and the width decreased with increased saturation. This finding suggests that surface curvature is not the only determinant of filling rate with increasing pressure. Image analysis using auto-correlation function and percolation-based algorithms suggest that there may be significant differences in the degree of correlation of the spatial arrangement of T_2 values between partially and fully saturated pellets. This finding is suggestive of some long-range, pore-pore interaction on adsorption.

PGSE NMR has also been used to study the morphology of the adsorbed water ganglia over length-scales ($\sim 10\,\mathrm{mm}$) lower than the MRI pixel resolution and diffusion was found to be unrestricted even at low saturation levels. This is consistent with long range correlations in adsorption behaviour in partially-filled

samples.

O8 Loading-Dependent Transport Properties of Zeolitic Imidazolate Frameworks Probed by In-Situ PFG NMR

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This presentation is focused on an emerging class of Metal-Organic Frameworks (MOFs) that is attracting worldwide attention: Zeolitic Imidazolate Frameworks (ZIFs). ZIFs constitute a novel subclass of Metal-Organic Frameworks, and are among the most promising MOF candidates for practical uses in gas separations and catalytic reactions due to their excellent stability and rich structural diversity. ZIFs are reported to possess unique properties for applications in storage, sensors, separations and catalysis. While we foresee significant potential for catalytic applications, in early 2007 we began exploring ZIFs for separations first. Extensive characterization of several selected ZIFs confirms their high adsorption capacities (often significantly exceeding those of zeolites) as well as their high potential for iso/normal separations and the removal of CO_2 and C_2+ hydrocarbons from natural gas. The screening has also revealed some unique adsorption and separation-enabling behavior that could not have been anticipated from standard material characterization tools. Molecular transport through porous media is also highly critical, since it can significantly affect adsorption/desorption rates. Subtle differences in molecular diffusion rates may be utilized to affect kinetic-based molecular separations for systems with low equilibrium selectivity. Therefore to maximize operational performance, most separation and catalytic processes require a detailed knowledge of both molecular adsorption and diffusion and correlation between these properties. Our recently constructed In-Situ Pulsed Field Gradient (PFG) NMR unit enables the study of a wide range of thermodynamic conditions (e.g. pressures and temperatures) in order to vary and control loading of guest molecules in porous materials in-situ, during NMR and PFG NMR experiments. This provides us with the unique capability to simultaneously study both kinetics and equilibrium conditions for single or multi-component molecular sorption and molecular diffusion at given loading, with values ranging from $10 \times 10^{-15}\,\mathrm{m^2/s}$ up to $10 \times 10^{-7}\,\mathrm{m^2/s}$. Initial application of this new capability to recently discovered ZIFs materials will be discussed; as these unique materials exhibit a high degree of structural flexibility at ambient conditions, and demonstrate unique adsorption and transport characteristics not yet reported in the literature.

O9 Micro- and Nanostructure of Polyelectrolyte Multilayers as Visualized by Water Spin Relaxation and PFG Diffusion

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Polyelectrolyte multilayers (PEM), prepared as ultrathin polymer membranes by alternating self-assembly of polycations and polyanions, have unique properties and are interesting in filtration processes and as membranes in electrochemical applications. Their structure and composition is controlled by the self-assembly process, which yields a disordered, hydrated polymer network with water voids of nanoscale size. Detailed structural information on ultrathin films is hard to yield by NMR methods, approaches to enhance sensitivity are the preparation of films on colloidal templates, or alternatively the preparation of stacked layers.

The latter approach is chosen in this work to investigate the lateral diffusion of water in planar films by pulsed field gradient diffusion NMR. The dependence of the mean square displacement on the observation time does not agree to Gaussian diffusion, suggesting restricted diffusion in a porous structure. However, the extraction of a pore size in a model of restricted diffusion yields a very large pore size of several micrometers, which is unexpectedly large in an ultrathin film. Therefore, the additional influence of cross-relaxation of water and polymer spins is investigated in Goldman- Shen experiments. These demonstrate a strong influence of cross-relaxation rates on diffusion echo decays, such that pore sizes obtained from the model of restricted diffusion have to be corrected. Corrected pore sizes are about $4\,\mu m$, and reflect the existence of domains of lower polymer density and thus faster water diffusion. These heterogeneities occur upon PEM preparation at high salt content for large layer numbers, and are detected in the surface morphology too. With increasing relative humidity the water dynamics is enhanced, and cross-relaxation rates reduced. This is consistent with a swelling process, where the pores are widening and subsequently filled with a larger water content.

In summary, polyelectrolyte multilayers with a local nanoporosity, as for example demonstrated earlier by cryoporometry [1], can additionally exhibit structural heterogeneities on the micrometer scale [2].

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4.3 Fluids in Porous Media (Including Supercritical and Complex Fluids)

$\boxed{\text{O10}}$ Determination of the Spatial Location of Coke in Catalysts by a Novel NMR Approach

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Standard heterogeneous catalyst characterisation techniques, such as gas adsorption and mercury porosimetry, only account for the structural heterogeneity of the catalyst surface. They completely ignore the chemical heterogeneity effects. Thus, most pore space descriptors, such as BET surface area, BJH pore size distribution, mercury porosimetry surface area, etc., are not necessarily accurate. Coked catalysts create a major change in the chemical heterogeneity of the surface and accurate characterisation is essential for understanding the catalyst deactivation processes. The need for a characterisation technique that accounts for the physical and chemical heterogeneity of the catalyst surface is an issue that remains to be resolved. Further, it is a problem that spans all porous media, including catalysts, adsorbents, reservoir cores etc.

A novel multi-component adsorption technique is proposed in this work that delivers a step-change solution to the aforementioned limitations. For example, a predominantly hydrophilic liquid would be attracted to the fresh regions of the catalyst surface, while a mainly hydrophobic liquid would be attracted to the regions covered by coke. The experimental procedure involved the co-adsorption of immiscible liquids (cyclohexane and water) on a model silica catalyst support at 298 K. Capillary displacement of cyclohexane by water was observed over a two week period with the aid of a Bruker 400 MHz NMR spectrometer. The evolving saturation levels, self-diffusion coefficients, and T_2 relaxation times, of the two liquids were studied. The long time saturation levels showed the presence of entrapped cyclohexane ganglia. These results were compared with corresponding data from mercury porosimetry. Entrapment of liquids usually takes place due to mass transfer limitations and these regions can be associated with the formation of coke. Self-diffusion coefficients provide information on the interconnectivity of pores and the mechanism of displacement, while T_2 values are dependent on pore size. Analogous experiments were also conducted with fresh catalysts, pure carbon materials and coked catalysts. It was found that the temporal evolution of the relaxation and diffusion data showed differences between the three types of samples. These data were analysed to determine the spatial location of coke and its effects on the pore size distribution in the spent catalyst. Evidently, this novel approach takes the wettability of the surface into consideration. It is therefore a method that accounts for the chemical heterogeneity of the surface and has the potential to determine the spatial distribution of coke unlike standard catalyst characterisation methods. Hence, the

use of NMR and co-adsorption of two immiscible liquids is proposed as a new catalyst characterisation technique that accounts for the physical and chemical heterogeneity of the catalyst surface.

O11 Memory Effects in Confined Fluids

Sergej Naumov [1], *Jörg Kärger* [1], *Rustem Valiullin* [1], *Peter A. Monson* [2]
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Disordered materials are widely used in many processes of industrial and environmental importance. The equilibrium and dynamic processes that occur in the pore space of these materials are strongly influenced by the confinement and the geometrical disorder of the porous matrix.

An inherent property of mesoporous materials is the occurrence of the sorption hysteresis. This means that the adsorption and desorption isotherms do not coincide over a certain pressure interval. The hysteresis in random porous matrices is largely affected by the geometric disorder in the pore structure, leading to a multitude of metastable states. Thus, during adsorption and desorption the system evolves in accordance with the respective rugged free energy landscape in an activated manner. These metastable states possess very long life times, thus making the equilibration of the system impossible on the experimental time scale [1].

The self-diffusion coefficient, as measured by PFG NMR simultaneously with the sorption experiments, also shows a well pronounced hysteresis behavior. Even for identical amounts of molecules inside the porous matrix one observes different values of self-diffusion coefficient on the adsorption and the desorption branches depending on the history how a given state had been attained. Performing incomplete filling/draining cycles on such mesoporous materials, one may compile a whole map of diffusivities, which reflects different distributions of the adsorbate under spatial confinement [2].

Thus, using PFG NMR, we provide direct experimental evidence that, within hysteresis loops, states with the same average fluid density may be characterized by the different average self-diffusivities. Therefore, we suggest that molecular diffusivity may be considered as an excellent probe of the history-dependent states of the confined fluid.

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O12 MRI of Contrast Agents in Porous Media

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Characterizing and modeling fluid flow in porous media is vital to understanding many important applications including oil recovery, chemical reactors, contaminants and water transport in soil. Contrast agents have been used to label fluid fronts or to image the flow and dispersion of the tracer itself. This method is relatively simple to implement and robust to characterize motion, especially in slow flows. We show that this method can be used quantitatively to understand flow field by an excellent comparison between theoretical hydrodynamic calculations and measurements. We have used this approach to understand the behavior of engineered tracers (such as functionalized nanoparticles) in porous media.

Flow experiments in porous media are often performed for simple geometries, such as one-dimensional flow in a rock core or bead pack. However, when flow field is larger than the aperture of the fluid source or drain, such as flow around a wellbore, geometry effects dominate the flow creating a wide range of velocities, pressures and capillary numbers. We have created a semi-spherical flow model with a small injection port into a large rock sample. We use MRI to image flows for a series of injection volumes, and hydrodynamic theory to predict the invasion front assuming that the flow obeys Darcy's Law. We will show the complex flow field in such a model and an excellent match between the theory and our experiments. This agreement shows that our MRI flow imaging can be used quantitatively to interpret the flow field and thus to study complex flow geometries and to understand complex flow in real rock due to porosity and permeability heterogeneity. Examples of single and multiphase flows in non-trivial geometries will be discussed.

Many functionalized contrast agents have been tested in medicine for identification of cells and tissues. We explore the use of such agents for studying geological samples. Such agents could offer sensitive detection for local environments or flow, for example, factors like temperature, pressure, salinity, surface properties, and pore structures. MRI can comprise a powerful technique to understand the movement retention and distribution of these nanoparticles in rock cores in order to understand, model, and control their behavior in porous media. We will show time resolved flow images of nanoparticles in sandstones, carbonate rocks, loose packs of sand and carbonate grains, as well as diagnose problematic behaviors such as the undesired retention of the nanoparticles.

O13 Multiscale Dynamics of Ionic Liquids Confined in Ionogel Membrane for Lithium Batteries

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Ionic liquids are known for their appealing properties such as high ionic conductivity, negligible vapour pressure, thermal stability, none-flammability and wide electrochemical stability window[1]. These properties lead to a broad field of applications such as optical devices, catalysts, sensors and electrolyte membranes[2]. They have recently been used as electrolytes in solar and fuel cells[3,4] and lithium batteries[5]. For such applications, these ionic liquids have been immobilized in a solid matrix[6,7] leading to composite materials called ionogels. However, the molecular dynamics of these liquid-like ions within a disordered solid matrix is still unknown.

Here, we choose the 1-butyl-3-methylimidazolium bistrifluoromethyl-sulfonylimide [BMI] [TFSI] as an cation-anion pair of ionic liquid confined within a silica-like mesoporous matrices made by a sol-gel route from hydrophobic methyl groups precursors (ionogels made from tetramethoxysilane, methyltrimethoxysilane; lithium salt Li TFSI was added). The Li cation, the proton-bearing cation [BMI], and the proton-free anion [TFSI] temperature dependence dynamics are investigated by a multiscale NMR approach of ^{7}Li, ^{1}H and ^{19}F respectively. We use high field spectroscopy and relaxation NMR at $8.6\,T$ to characterize the microscale dynamics. The mesoscale dynamics is followed by nuclear magnetic relaxation dispersion (NMRD) between $10\,kHz$ and $20\,MHz$ [8,9]. Pulse Field Gradient measurements allow investigating the macroscale dynamics. In order to illustrate the drastic impact of the confinement on the ionic dynamics, we report studies of both the ionogel and the ionic liquid alone.

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O14 Permeability Mapping in Porous Media with Magnetization Prepared Centric-Scan SPRITE

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The concept of permeability is central for hydrocarbon recovery from petroleum reservoirs and for studies of groundwater flow in aquifers. Spatially resolved measurements of permeability are of great significance for fluid dynamics studies. A variety of magnetic resonance methods have been employed for prediction of permeability in non-flowing systems. These measurements, through correlations, are particularly important for downhole NMR logging measurements in petroleum reservoirs. For complex objects with macroscopic heterogeneities, bulk measurements will be unreliable and we prefer flow based measurements with spatial resolution. Quantitative porosity and mean velocity maps would allow reconstruction of a quantitative permeability map for »parallel circuit« systems. A convenient concept of local Darcy's law is suggested. The product of porosity, W, and mean velocity, $\langle V \rangle$, images in the plane across the average flow direction is directly proportional to permeability, k:

$$k(x, y) = W(x, y) \cdot \langle V \rangle(x, y) \cdot \nu \cdot L \cdot P^{-1},$$

where ν - dynamic viscosity, L - length of the sample, P - total pressure drop.

The proposed approach is well suited for description of data obtained with non-slice-selective 2D centric-scan SPRITE. Single Point Ramped Imaging with T_1 Enhancement (SPRITE) permits reliable quantification of local fluid content and flow in porous media [1-6]. It is particularly advantageous for reservoir rocks characterized by fast magnetic relaxation of a saturating fluid. Velocity encoding using the Cotts pulsed field gradient scheme [7] improves the accuracy of measured flow parameters. The method is illustrated through measurements of 2D permeability maps in a capillary bundle, glass bead packs and composite sandstone samples. Permeability measurements performed on model porous samples showed excellent agreement with conventional steady state flow measurements and theoretical predictions.

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O15 Transport and High-Pressure Phase Equilibria in Mesopores

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Heterogeneous catalysis in high-pressure environments is a standard process in state-of-the-art industrial chemical synthesis. Micro- and mesoporous materials are widely used as hosts for the catalysts, while educts and products are delivered and removed under high pressure conditions. The supercritical state is here of particular interest because of its superior dynamical properties such as low viscosity, no surface tension and high diffusivity. Recently, Valiullin et al. have shown that pulsed field gradient nuclear magnetic resonance spectroscopy (PFG NMR) is a particularly suitable tool to probe diffusion properties of sub- and near-critical fluids in mesopores [1]. The experiments performed have been designed to probe diffusivities of intra-porous fluids as a function of temperature under isochoric conditions. The thus measured diffusivities have shown a step-like change at a temperature below the bulk critical temperature. This change has been anticipated to be related to the pore critical temperature.

To further validate these results, a complete phase diagram and its interrelation with the transport properties would be of particular importance. To be able to do this, however, the experimental scheme has to be redesigned to operate under isothermal conditions with variable pressure. In this work, we present an experimental setup we have designed to suit this purpose and some results obtained in this way. In particular, a special NMR sample vessel has been constructed which permits to maintain pressures up to 200 bars. A check valve, connecting the NMR tube made of PEEK material and external reservoirs, is designed to allow activation of porous samples in the NMR tube and to load it with different mixtures of gases and liquids at different pressures.In this way, it is possible to measure pressure-dependent self-diffusivities of organic compounds solved in supercritical solvents, e.g., in carbon dioxide in the bulk state as well as in the mesopores. Results on diffusivities of sub- and supercritical toluene - CO_2 and ethane - CO_2 mixtures in mesoporous host materials will be presented and discussed by correlating them with the respective phase diagrams.

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4.4 CMMR 10

O16 **Temperature-Compensated Portable Magnet Built from Permanent Magnetic Materials**

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Mobile NMR sensors use small magnets that can be carried along to the site where the measurements are required. To satisfy this demanding condition magnets are built from permanent magnetic materials mainly because of robustness, compactness, and costs.For a long time the inherent errors in the polarization of such materials leaded to magnets generating inhomogeneous magnetic fields, and this was accepted as the price to be paid for mobility. During the last years important progress has been reported in the development of mechanical shimming techniques suitable to homogeneize the magnetic field to the limit required to resolve the spectra of protonated molecules[1,2]. However, the major challenge imposed by the strong temperature dependence of the remnant magnetization of permanent magnets still remains unsolved. Depending on the magnetic material, a temperature variation of just one degree °C leads to a drift in the resonance frequency of several hundreds of ppm restricting the range of applications of mobile sensors to labs with controlled conditions.

In this work we present the design and construction of a mobile sensor with negligible drift in the resonance frequency induced by changes in temperature. This is obtained by opposing the fields generated by pieces made of two magnetic materials with different thermal coefficients, like NdFeB and SmCo. The condition to be fulfilled requires that the ratio of fields generated by each material matches the ratio of the thermal coefficients[1]. Using this approach a magnet generating a field of 0.25 T was temperature compensated obtaining a positive temperature coefficient of 1.8 ppm/°C. The change in the sign of the coefficient shows the presence of a zero crossing, which could be further approached by varying the field ratio with higher accuracy.

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O17 **Mobile NMR Systems for Antarctic Sea Ice Studies**
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Sea ice plays a significant role within the global climate system and therefore work has been undertaken to understand this vast material. In winter, the oceans in the polar regions freeze to form a layer of sea ice several meters thick and in Antarctica thisgrows to an area of approximately 20 million square kilometres. The bulk of this ice is referred to as congelation ice and consists of

a matrix of interconnected brine filled pores. In some regions of Antarctica, sea water circulating under the ice shelves is further cooled and produces a stream of ice platelets that cling to the bottom of existing congelation ice causing the sea ice to continue to grow in thickness. Compared to congelation ice, the incorporated platelet ice has very different mechanical, electrical and thermal properties, pore structure and also large spatial variations due to the variability of the ocean currents and structure of ice shelves. To date there is no method available that can easily distinguish between the various ice types and that can obtain information about the brine pores. NMR has the potential to fulfil this need.

A NMR sensor system has been developed to measure the brine fraction and diffusion of brine contained within Antarctic sea ice. The system is based on a $0.3\,\mathrm{T}$ Halbach permanent magnet array that was constructed from a series of rectangular magnets placed within aluminium rings and then surrounded by thermal insulation, heating tape and a strong metal housing to provide temperature stabilisation and robustness which is necessary in the cold and harsh Antarctic environment.

Brine fraction experiments with this new apparatus were performed in November 2009 near Ross Island, Antarctica and were our first successful attempt at using permanent magnets in Antarctica. The results obtained agreed well with the traditional temperature/salinity determination method and our earlier Earth's field system. The advantages of the NMR technique are that it is a direct method and it has the ability to obtain data within minutes compared to several hours with the traditional method. The advantage of the Halbach system compared to our Earth's field system is the vast increase in signal to noise.

Some initial diffusion data was obtained and demonstrated the potential of the system in obtaining pore information. Further refinements have been undertaken to the Halbach system and experiments to increase the sensitivity and should guarantee better and more complete results next time.

O18 NMR Halbach Permanent Magnet System for Antarctica

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Naturally grown ice is often porous due to impurities or the growth process: Annual sea ice is especially inhomogeneous and it's pores are filled with water due to the salinity of the sea water.

A rock core analyser type NMR instrument was recently deployed to Antarctica:

It consisted of 160 permanent magnets, which were stacked in 10 aluminium rings to a cylinder with an inner diameter of $120\,\mathrm{mm}$ and height of $265\,\mathrm{mm}$. By arranging the magnets in a Halbach array manner, a sufficiently homogeneous B_0 field of $0.28\,\mathrm{T}$ ($12\,\mathrm{MHz}$) is created in the middle with a very weak stray field

outside.

In addition two pulsed field gradient coil sets were fitted into the bore: The dipolar coil provides a transversal gradient of $21.7\,\mathrm{mT/m/A}$. The quadrupolar coil yields $22\,\mathrm{T/m/A}$ for a longitudinal gradient.

The sample bore is $35\,\mathrm{mm}$ wide and is aligned with the Halbach cylinder axis. Around its centre a solenoidal RF coil of $86\,\mathrm{mm}$ height, consisting of two parallel wires with 17 turns, is wound. The resonance line width can be tuned from approximately $10\,\mathrm{MHz}$ to $13\,\mathrm{MHz}$ with a typical width of $20\,\mathrm{kHz}$.

To prevent drift of the magnetic field due to temperature variation it is essential to stabilize the permanent magnet's temperature: Therefore an electrical heat tape is wrapped around the aluminium structure before it was mounted into a steel bin using fitting foam. Another layer of insulation and a copper RF shield has been inserted between the pulsed field gradient coils and the B_1 coil. Foam slabs on top and the bottom complete the thermal insulation. The temperature is kept constant by a PID controller which is connected to a temperature sensor in the middle of the aluminium structure. The sample bore and tuning rods are easily accessible from top.

The total weight of the magnet system is $58\,\mathrm{kg}$.

The instrument was driven by a Kea 2 NMR spectrometer from magritek together with a BAFPA 40 gradient amplifier from Bruker and a standard notebook.

Cores of the diameter of $23\,\mathrm{mm}$ were taken from all depths of the annual sea ice sheet ($2.2\,\mathrm{m}$) near Cape Evans, Ross Island. To thermally insulate them and to keep the instrument clear of snow dust, the cores were slid into fibre glass tubes before they were inserted into the sample bore.

The brine/volume fraction and T_2 for the cores were determined, furthermore diffusion measurements of the brine were attempted. The detection of the weak brine signal was enhanced by CPMG like pulse sequence extensions.

O19 A Consistent and Systematic Approach to the Design, Fabrication and Testing of Permanent Magnets Applied to Single-Sided NMR

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Permanent magnet-based NMR has been a continuously developing field in the past 15 years due to its attractive portability, lack of maintenance need and lower cost. One major challenge of such magnets is the achievement of high field homogeneity. While several prototypes have recently been reported to achieve sub-ppm homogeneity, the volume of interest has always remained small compared to the magnet size. In addition, few systematic approaches to the design of such magnets have been proposed. We have introduced in the past an analytical method for the design, fabrication, characterization and shimming of permanent magnets [1,2], based on the well-known technique of spherical harmonics expan-

sion of the magnetic potential and of the field components. This framework can be applied to in situ and ex situ magnets to realize desired field profiles such as highly homogeneous fields, or strong constant gradient. We concentrate here on the design and realization of single-sided magnets. We will give a theoretical analysis of the problems of the remote homogeneous field and of the remote constant gradient, along with the issues of high precision field measurements in strong gradients. A first prototype generating a gradient of $3.3\,\text{Tm}^{-1}$ with a field of $0.33\,\text{T}$ (^{1}H frequency of $14\,\text{MHz}$), $2\,\text{cm}$ away from the surface of the magnet has been fabricated and tested. The diameter of the magnet is $20\,\text{cm}$ with a height of $12\,\text{cm}$, for a weight of about $40\,\text{kg}$. We experimentally achieved variations of less than $100\,\text{ppm}$ in planes parallel to the surface of the magnet in a region of $8\,\text{mm}$ diameter and $6\,\text{mm}$ height. This corresponds to a 1D resolution better than $10\,\mu\text{m}$ in this entire volume. We will also propose a new RF surface coil design generating a field parallel to the coil plane with optimal sensitivity at a given penetration depth. Using these coils and the magnet prototype, we were able to record NMR spectra for the purpose of relaxation measurements and 1D tomography.

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O20 Polymers Under Mechanical Stress - an NMR Investigation

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While there is chain order in the crystalline region of semicrystalline polymers, there is disorder in the amorphous regions as well as in elastomers and polymer melts. Mechanical stress can result in partial chain ordering of the disordered polymer chains.

The local order and the molecular dynamics in polymers under mechanical stress is studied by low-field NMR. Low-field NMR magnets using a Halbach arrangement have a rather confined stray field and permit the application of NMR in a stretching apparatus and a rheometer. The major drawback of low-field NMR, the lack of chemical shift resolution, is not a problem, because in the study of known materials properties other than their chemical composition are of interest. A Halbach magnet of $0.75\,\text{T}$ has been used resulting in a Larmor frequency of $32\,\text{MHz}$ for protons.

Stretching elastomers results in drastic changes in the chain arrangement,

which results in a reduction of the mobility of the polymer chain segments. The resulting stronger residual dipolar couplings show up in the stronger buildup of double quantum coherences. The transverse relaxation shows a two component behavior, typical for many polymers. The slower relaxing component becomes significantly shorter on stretching indicating reduced mobility of the chain segments.

The crystalline and amorphous fractions of semicrystalline polymers are distinguished by their transverse relaxation times. Under mechanical load there is a significant shortening of the transverse relaxation time, which partially relaxes with time, when the load is kept constant. This nicely correlates with the relaxation of the mechanical stress as a result of the rearrangement of the polymer chains.

Polymer materials often contain inorganic fillers The interaction with paramagnetic moieties in the fillers in polymer nanocomposites has a strong impact on the longitudinal relaxation time. Delaminating filler particles under mechanical stress results in a shorter T_1 of the protons in the polymer, because the contact area between the filler and the polymer increases.

Shear on a polymer melt in a Couette cell applied results in ordering of the polymer chains. This shows in residual dipolar coupling measured in the double quantum buildup similar to the results on stretched elastomers. The molecular mobility in the melt as a function of the temperature is conveniently probed by the transverse relaxation time.

O21 Single-Shot Depth Profiling with a Single-Sided NMR Sensor

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The optimization of single-sided magnets for sample profiling points to improve the uniformity of the static gradient maximizing at the same time the ratio B_0^2/G_0 that defines the sensitivity. Typical magnet geometries provide the best performance for large B_0 values when also a large G_0 is obtained. In this limit, the thickness of the excited slice becomes extremely thin (of the order of $100\,\mu$m) requiring mechanical or electronic slice repositioning to profile large depth range into the sample [1].

In this work, a U-shaped magnet was equipped with a shim unit made of permanent blocks [2] intended to strongly reduce the magnetic field gradient along the depth direction while keeping under control the lateral field. Under these conditions depth profiles over a range of two millimeters are measured with a resolution better than $50\,\mu$m in a single-shot as the Fourier transform of the echo signal acquired in the presence of a static gradient of about $2\,$T/m. The increment in the thickness of the sensitive volume eliminates the need for repositioning the sensor with respect to the object allowing us to cover the

whole depth range in a single measurement. An important advantage of this new magnet design is that - by a proper design of the shim unit- the reduction in the static gradient is not achieved at the expense of a strong reduction in the magnitude of the static field, a price usually paid in conventional designs. The field of this prototype is about $0.2\,T$, which is comparable to the field generated by previous sensors of the same size [1].

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4.5 Hyperpolarization

O22 **Real-Time Detection of Polymerization Reactions with Hyperpolarized Xenon at Low Magnetic Fields**

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For process control it is desirable to develop simple devices for studying polymerization reactions in real-time and in-situ. We are demonstrating an approach using NMR at fields as low as $39\,G$ and hyperpolarized Xenon, which allows us to observe polymerization reactions in real-time. The investigated reaction is a free radical polymerization with the initiator azobisisobutyronitrile (AIBN) and the monomer methyl methacrylate (MMA). AIBN and MMA are mixed together in a sample tube under noble gas atmosphere, and the reaction is started by irradiation with UV light ($360\,nm$). As the reaction goes on, it is possible to acquire Xenon spectra that show increasing line broadening and a change of the chemical shift depending on the state of polymerization. This observation gives rise to the idea that a single-sided high resolution NMR sensor can be developed with which at least light induced polymerization reactions can be studied in-situ and in real-time.

4.6 Novel Techniques, Pulse Sequences, and Spin Dynamics

O23 **Strafi Micro-Profiling of Fast Relaxing Slow Moving Species - From cement to Confined Polymers**

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Recent developments of multidimensional diffusion and relaxation analysis have shown the importance, when studying porous media, of probing relaxation, diffusion and exchange in a wide range of dynamics, from 10^{-4} to $1\,\mathrm{s}$ [1]. In particular, drying or desiccation of non saturated porous materials is a complex phenomenon, especially in hydraulic systems such as cement. It involves funicular and pendular processes in a reactive matrix and is not always fully understood. Further spatially resolved experimental data are still clearly needed. However probing the spatial distribution, at the micron scale, of rigid or slow moving species in a fast relaxing porous environment remains a challenge. Indeed, strong pulsed gradients often results in gradient dead times in the range of milliseconds, while hydrates may have relaxation rates in the range of $10^{-4}\,\mathrm{s}$. It is well known that the use of static gradients allows circumventing this difficulty [2] but the spatial resolution and the sensibility is limited [3].

To that respect, we have optimized a home-made Stray field experiment. An antenna was specifically designed to deliver a maximum of radio frequency power (about $200\,\mathrm{W}$ during $3\,\mathrm{ms}$) concentrated within the thin slice geometry of the STRAFI plane, while maintaining a short probe dead-time of $10^{-5}\,\mathrm{s}$ and an open geometry. This design allows the observation of solid protons and the measurement of slow diffusion coefficient ($10^{-13}\,\mathrm{m^2/s}$) with motion encoding time of only a few $10^{-4}\,\mathrm{s}$. We will show how we were able simultaneously to profile the relative distribution of solid hydrates and mobile water and to profile the relaxation dynamics of water in the pores of a Portland cement with a spatial resolution of $10^{-5}\,\mathrm{m}$. To our knowledge, this combination of short encoding time and high spatial resolution is not accessible with other existing experimental setups. Finally, by drawing our recent study of polymer melts confined in porous geometries, we will show how we were able to probe slow diffusion coefficients in the range of $10^{-13}\,\mathrm{m^2/s}$ for species with short T_2's (a few $10^{-4}\,\mathrm{s}$).

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O24 MAS PFG NMR Studies of Mixtures in Porous Materials

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Magic Angle spinning (MAS) NMR and pulsed field gradient (PFG) NMR both are well established and fundamental methods in physics, chemistry and material science nowadays. While MAS NMR is able to reduce line broadening in NMR spectra due to dipolar interactions, PFG NMR is capable to study molecular transport and diffusion phenomenas.

Here we report on the application of both methods simultaneously for the investigation of single molecule species as well as mixture diffusion in porous materials such as metal organic frameworks (MOF). The combination of the two methods proves to be particularly beneficial for this class of guest-host systems, since static PFG NMR, although generally capable of investigating mixture diffusion [1] in porous systems, is still limited by line broadening. However, limited mobility of the molecules adsorbed calls for the need of sufficiently high pulsed field gradients. Gradient systems provided with commercially available high resolution MAS probes do not provide the necessary gradient strength. Therefore, we used a 3D imaging gradient system Micro2.5 (Bruker) providing gradients of up to $1.5\,\mathrm{T/m}$ in each direction in combination with a narrow bore high resolution MAS probe in a modular setup. By using all three gradient coils at the same time with the same current, a resulting gradient in the magic angle is generated, thus allowing the investigation of diffusion along the rotational axis of the sample [2].

The combination of MAS and PFG techniques is by no means standard in current NMR studies. We introduce methods for the proper alignment of the MAS probe in the gradient system, in order to avoid the influence of sample rotation to the determined displacements along the sample axis. Finally, first results of single species and mixture diffusion in model systems are presented and interpreted.

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O25 MR Imaging Inside Metallic Vessels

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We introduce MRI inside macroscopic conductive metallic vessels [1]. Until now Fourier transform MRI has been impossible inside metal vessels due to eddy currents induced in the vessel walls by switched magnetic field gradients. These eddy currents corrupt the magnetic field gradient experienced by the sample,

with associated deleterious effects on spatial encoding. We have solved the eddy current problem in metal vessels and generated high quality images by employing the magnetic field gradient monitoring (MFGM) [2] method. The MFGM method permits facile determination of the experimental magnetic field gradient waveform in the sample space. Knowledge of the true gradient waveform permits simple post processing of k-space data and reconstruction of high quality images.

The metallic vessel under study was an aluminum vessel length 15 cm, o.d. 7.6 cm, with a 1.3 cm thick wall. The vessel was centered along the B_0/G_z axis inside a microimaging gradient set in a 2.4 T 32 cm horizontal bore supercon magnet. The imaging RF coil, fit inside the cell, was a homebuilt birdcage (i.d 3 cm). The MFGM [2] measurement employed a NMR microprobe to measure the magnetic field gradient waveform. Knowledge of the magnetic field gradient waveform permits determination of the MRI k-space coordinates. Our test sample was a simple polymer resolution phantom with holes and slots cut to various sizes. MFGM measurement of the 64×64 Spiral Sprite waveforms (G_x and G_z) permitted determination of the true k-space coordinates of the SPRITE waveforms. Eddy currents in the form of linear gradients and static field shifts $B_o(t)$ were observed corrected. Eddy current effects near the k-space origin grossly alter the k-space data coordinates.

We employed the incorrect k-space samples, of known k-space coordinates, to estimate the Cartesian samples required for FFT image reconstruction. A variety of re-gridding strategies may be employed for this procedure, but a simple interpolation gave satisfactory results. Without post processing, the phantom image is catastrophically corrupted by the aluminum vessel. With MFGM guided post processing, and FFT, a high quality image is generated. The image quality is near identical to that obtained in the absence of the metal vessel.

High-pressure NMR spectroscopy plays an indispensable role in numerous science fields. This work will permit the extension of high pressure NMR studies to MRI. MRI compatible pressure vessels fabricated from aluminum, titanium or non-magnetic stainless steel are now feasible. Such vessels will open new vistas of study for material science MRI, including methane hydrate formation and CO_2 storage, to name but two very active scientific fields of contemporary importance. Early examples of such studies will be presented.

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O26 Measurement of Oscillatory Motion in Fluids

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Magnetic Resonance Elastography (MRE) measures an elastic material displacement amplitude in a sound field via the signal phase accumulation as a function of the displacement and the magnetic field gradients oscillating in sync

with the periodic excitation. The usual applications of MRE include a measurement of the shear modulus in a living tissue or gel-like substances.

The goal of this project was to develop an MRI technique to image a periodic motion in fluids for studies of cavitation, turbulence, thermoacoustics, and fluid flow in media. Although a fluid does not have any shear strength that a gel does, it can still oscillate via a rotational motion in the eddy currents in a turbulent liquid, in a flow through granular/porous media, by a strong acoustic field in a gas or by the motion of cavitating bubbles.

In this project, the concept of MRE was applied to measure the displacements at a range of gradient frequencies with the goal to obtain power spectra of the oscillations. We used a set of the oscillating gradient waveforms ($16\,\text{Hz}$–$10\,\text{kHz}$) during the preparation part of the sequence with the Z-storage of X- and Y-components of the transverse magnetization with the subsequent use of the spiral SPRITE imaging as a readout sequence. A major problem with applying the ideas of MRE to liquids is the presense of flows that, in case of oscillating gradients, will contribute a non-zero phase. To cancel the flow effect, velocity-compensated symmetric oscillating gradient waveforms were used. The technique was applied to studies of cavitating liquids and a gas in a working thermoacoustical device.

O27 Observing Diffusion-Diffraction Patterns in Heterogeneous Specimens Using the Double-PFG NMR Methodology

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Diffusion-diffraction patterns arising from restricted diffusion are extremely important for characterizing pore morphology. In conventional single-PFG (s-PFG) NMR experiments, pore size can be directly inferred from the minima of $E(q)$ profiles; however, these diffraction troughs are lost in s-PFG when (a) compartments are polydisperse in size, (b) when locally anisotropic pores are randomly oriented and (c) when pores are inhomogeneous. These scenarios are predominant in many porous media found in nature.

The double-PFG (d-PFG) methodology1 is emerging as a powerful technique that can potentially overcome the inherent limitations of s-PFG NMR. Recent theoretical contributions [2] have provided exact solutions for restricted diffusion in d-PFG NMR, and predicted the existence of zero-crossings of the signal, $E(q)$. These zero-crossings were predicted to persist even when pores are highly heterogeneous in size or shape.

Here, we experimentally challenged the predictions of the novel theory. We conducted s- and d-PFG NMR experiments on controlled porous media in which the ground truth is known a priori. Water-filled microcapillaries with well known nominal inner diameters (ID) of various sizes were mixed to construct specimens with increasingly broadening polydispersity. Alternatively, microcapillaries were cut or crushed into very small shards to achieve a random orientation. Scanning

Electron Microscopy (SEM) verified that these cylindrical pores were indeed randomly oriented. The resulting porous medium was highly inhomogeneous with a line width of $\sim 0.5\,\mathrm{kHz}$; therefore, all s- and d-PFG experiments on randomly oriented pores were conducted using bipolar gradients.

Our findings [3] show that indeed, when pores are characterized by a distribution of either size or orientation, the diffusion-diffraction minima in s-PFG disappear. On the contrary, when d-PFG NMR experiments were performed, the zero-crossings persisted for both polydisperse and randomly oriented specimens. For the polydisperse specimens, we found that the q-value of the zero-crossing and its rate of return to the ambient background noise level can be used to infer on the average size of the distribution and its width. For randomly oriented porous media, the zero-crossings were experimentally observed for several different IDs, and the accurate sizes could be extracted, but only when using bipolar gradients.

Our results suggest that bipolar d-PFG NMR is the method of choice for studying heterogeneous specimens. The zero-crossings can be used to measure pore size and infer on the presence of restricted diffusion, a difficult task considering the presence of internal gradients. Our results validate the theory and demonstrate that novel microstructural features can be obtained using bipolar d-PFG NMR.

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O28 Improving Estimates of Nuclear-Spin Relaxation Time (T_1) in Surface-NMR Experiments

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Surface nuclear magnetic resonance (NMR) is a relatively novel and powerful geophysical technique for investigating hydrological characteristics of shallow aquifers from the Earth's surface in a non-invasive way. Large current loops of approximate 100 m diameter are laid on the ground to transmit electromagnetic pulses into the subsurface. These pulses excite spins of protons in groundwater molecules out of their equilibrium state in the Earth's magnetic field. The spin response is recorded on either coincident or offset surface receiver loops of similar dimension. The amplitudes of the response signals recorded after single-pulse excitation provide estimates of water-content in the shallow subsurface. Another important parameter is the NMR relaxation time T_1, from which information on pore structure or even hydraulic conductivity can be inferred under favourable circumstances. T_1 data are conventionally acquired using a scheme that involves two sequential pulses of electromagnetic energy, the second of which is phase-shifted by π relative to the first. We show that variations of the excitation field with distance from the transmitter introduce a significant

bias in conventional estimates of T_1. Here, we propose a novel yet simple modification to the conventional scheme that is theoretically capable of resolving this problem. The proposed scheme comprises a conventional double-pulse sequence followed by an additional double-pulse sequence in which, for this latter sequence, the 2nd pulse is in-phase with the 1st pulse. Subtracting the voltage signals measured during the two double-pulse sequences eliminates the bias. This strategy of continuously cycling the phase of the 2nd pulse between π and 0 in sequential double-pulse experiments and then subtracting the resulting voltages is a promising step towards recording more reliable T_1 data under general field conditions.

O29 NMRDD and DISCORD: Novel Techniques to Study Relaxation Dispersion of Complex and Heterogeneous Fluids

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The study of the relaxation properties as a function of the Larmor frequency - or the dispersion - has long been recognized as a useful tool for probing the dynamic processes in complex fluids. With the advent of fast field cycling (FFC) techniques, the measurement of the dispersion became both faster and easier, opening up a wide range of applications. We present here two new FFC-based techniques developed specifically to study complex and heterogeneous systems, i.e., systems characterized by distributions of relaxation times associated with different groups of spins or different molecular species. In the first, termed NMRDD (nuclear magnetic relaxation dispersion of distributions), the relaxation behavior at each Larmor frequency is analyzed in terms of a distribution of relaxation times, and the evolution of this distribution is traced as a function of the frequency. In the second, termed DISCORD (dispersion correlation relaxometry of distributions), the distribution at one Larmor frequency is correlated with that at another frequency, generating a two-dimensional map that allows unambiguous separation of the different spin groups or exchange times between them which - despite their different dispersion characteristics - may be impossible to distinguish with the simple one-dimensional NMRDD.

One application of the NMRDD and the DISCORD is to systems that are mixtures of components or phases each characterized by its own dispersion relation. A simple example is an emulsion of two immiscible fluids, such as cheese, where fat droplets are suspended in a water-protein system. We found that while already the NMRDD showed a clear change in the shape of the relaxation distribution with the Larmor frequency, the DISCORD permitted a clear identification of the two fluids and, thereafter, the association of different sections of the NMRDD with each fluid.

Another application of both techniques is to complex systems whose dispersion is determined by the interactions between the different components of the mixture. In that case, the spectral density mapped out in the FFC experiment

encodes information not just about the dynamics of individual molecular species, their sizes and internal motions, but also about their mutual interactions. An important class of such fluids are heavy crude oils, which are complex mixtures of simple hydrocarbons, such as n-alkanes and small aromatics, and large polar macromolecules, known as resins and asphaltenes, with a tendency to aggregate and precipitate out of the solution. The NMRDD and DISCORD proved to be sensitive probes of the asphaltene aggregation state as well as of the strength of the interactions between the various smaller hydrocarbons and the aggregates.

More generally, any complex fluid system with a wide spectrum of correlation times in the range from 10s of micros to 10s of ns can be fruitfully studied with the NMRDD and DISCORD.

4.7 Porous Media in Medicine

O30 **Effective Medium Theory of Diffusion and Transverse Relaxation in Heterogeneous Media**

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Quantifying sample microstructure using MR is a challenging inverse problem: While the signal is typically acquired over a millimeter-size sample (voxel), the relevant structural information is found on the scale of micrometers (e.g. cell size in biological tissues). In MR, the sample's microstructure is embodied in the spatially varying relaxation rate, magnetic susceptibility, local diffusivity, and in the positions and orientations of membranes. The presence of these features defines how different the sample is from a uniform medium; in the language of transport theory, how disordered the sample is. A measured MR signal from a macroscopic voxel is effectively averaged over all local disorder realizations. It is at the level of this averaging that most of the structural information is lost. The practical question is, therefore, what are the microstructural features that are still accessible after this averaging and, hence, can be quantified by MR? To address this question, we develop [1,2] an effective medium theory (EMT) framework for the MR signal from a heterogeneous medium. Its central quantity is the propagator of the Bloch-Torrey equation, i.e. the evolution of the magnetization of a point source. In the frequency representation, it describes the spectral line shape in response to a diffusion-weighting gradient with a wave number q.

Technically, this propagator has to be averaged over the disorder realizations. The effect of disorder averaging is accumulated in the so-called self-energy part of the propagator [1,2]. This function replaces the conventional relaxation rate in the spectrum of a homogeneous fluid. The presence of microstructure results in a dependence of self-energy on frequency and q. The self-energy part is related

to the disorder correlation functions which embody all quantifiable structural characteristics after the voxel averaging. We show how the Taylor expansion of the self-energy part in q gives rise to the dispersive transverse relaxation rate [1], dispersive diffusivity (measurable by oscillating gradients), time-dependent kurtosis and higher cumulants [2]. Using the EMT approach, we consider transverse relaxation from a medium with spatially varying Larmor frequency [1], and the DWI signal from a medium with spatially varying diffusion coefficient [2].

The EMT approach shows that the information that survives the sample averaging includes the variance and the correlation length of the disorder in either local characteristic. The correlation length defines a time scale which should be probed by the measurement aimed at the microstructure examination. Explicit expressions for the relaxation and diffusion characteristics agree well with Monte Carlo simulations [1,2].

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O31 Axon Diameter Mapping of Pig Spinal Cord Using d-PFG Filtered MRI

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Introduction: White matter in the spinal cord consists of packs of long aligned nerve axons that conduct information between the brain and other parts of the body. The ability to measure an apparent fiber diameter and its spatial distribution within the spinal cord is of particular interest because axon diameter scales with the velocity with which information propagates along nerves. Double pulsed field gradient (d-PFG)-based sequences [1], in which two single PFG blocks are applied consecutively, can be used to measure microstructural features such as fiber diameter [2,3], cell eccentricity [4,5], and local anisotropy [6]. In this study, we mapped the apparent mean diameter within fixed pig spinal cord using d-PFG filtered MRI.

Materials and methods: A formalin-fixed pig spinal cord was rehydrated and put in a $10\,\text{mm}$ Shigemi tube (Shigemi Inc.) with the spine's white matter aligned with the z-axis of a $7\,\text{T}$ vertical-bore Bruker DRX system. To account for any deviation of the fiber orientation from the z-axis, a 21-direction diffusion tensor imaging (DTI) experiment was performed first with the parameters: $d = 3\,\text{ms}$, $D = 50\,\text{ms}$, G between 0 and $110\,\text{mT/m}$, and the imaging parameters were: TR/TE = $3000/59.3\,\text{ms}$, FOV = $11\,\text{mm}$, matrix size = 128×128, and slice thickness = $4\,\text{mm}$. Next, D-PFG filtered MRI was performed with the same imaging parameters except TR and TE, which were set to $3500\,\text{ms}$ and $7\,\text{ms}$, respectively. The two wave vectors were applied sequentially while the angle between them was varied between 0 and $360°$. The diffusion encoding pa-

rameters were: $d = 3.15\,\mathrm{ms}$, $D = 60\,\mathrm{ms}$, and G was between 0 and $664\,\mathrm{mT/m}$. A recently introduced theoretical framework [7], which makes it possible to calculate the MR signal attenuation due to restricted diffusion within a pack of cylinders, was fitted to the data by also taking into account a possible free water compartment [8]. A pixel by pixel analysis was applied to create a pore diameter map within the white matter region of the spinal cord.

Results and Discussion: The calculated fiber diameter from the d-PFG filtered MRI experiments range is from 3 to $5.5\,\mathrm{\mu m}$, which is the expected range for such a specimen [9]. The relative sizes of the axons generally follow the expected known anatomy of the spinal cord white matter. However, histological staining could help substantiate these findings.

Conclusion: d-PFG filtered MRI is a powerful tool for mapping the axon diameter, and potentially other microstructural features of tissues.

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O32 Diffusion Restricted by Permeable Membranes: Theory and Applications in Biological Tissues

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Restrictions to molecular motion by membranes are ubiquitous in biological tissues, porous media and composite materials. Recently we demonstrated [1] how the presence of permeable membranes gives rise to distinct features of transport. We consider diffusion restricted by flat randomly placed and oriented permeable membranes and focus on the disorder-averaged propagator, which is found by reformulating the transmission across a membrane as a scattering problem. Transmission across multiple membranes is described using the renormalization group technique. In this way, we find the frequency-dependent diffusivity for all frequencies, membrane surface-to-volume ratios and permeabilities. In particular, our solution reveals a universal scaling behavior of the diffusion coefficient for low frequencies (large diffusion times) with a characteristic square-root frequency dependence. Equivalently, the time-dependent diffusion coefficient approaches its tortuosity limit as the inverse square root of time. We relate this dispersive behavior to the return-to-origin probability of a random walker. Our theoretical results agree well with Monte Carlo simulations

in two dimensions.

To demonstrate how our model can be applied to identify the presence of permeable membranes in complex samples and to quantify membrane parameters, we analyze the two recent DWI experiments [2,3].

Kim et al. [2] measured the time-dependent diffusion tensor eigenvalues using a stimulated-echo DWI in ex vivo muscle samples for times between 30 and 800 ms. We demonstrate that the decrease of the eigenvalues transverse to the muscle fibers indeed follows an inverse square root time dependence. This previously unidentified behavior is the "fingerprint" of cell membranes acting as dominant restrictions to water motion. The values of membrane permeability and surface-to-volume ratio agree well with histology.

Does et al. [3] measured the frequency-dependent diffusivity in rat brain gray matter using the oscillating gradient technique. We show that the diffusivity [3] exhibits a square root frequency dependence in the whole range of frequencies, up to 1 kHz. Based on our model, the relatively large permeability and surface-to-volume ratio calculated from the data [3] is consistent with intracellular membrane-like restrictions, such as the endoplasmic reticulum, nuclear envelope etc. Our model shows that the effective permeability of these membranes decreases by about twofold in a globally ischemic brain, while their surface area remains practically unchanged. This permeability decrease is proposed as a novel biophysical mechanism for the diffusion coefficient drop in acute stroke.

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4.8 Porous Media in Environmental Science

O33 Magnetic Resonance Imaging in Real Soils: Water Content Measure and Microstructure Probe

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Magnetic Resonance Imaging (MRI) is frequently used for studying model porous media (sand, glass beads [1]) but is rarely used for studying undisturbed or repacked soils. In fact, these kinds of samples present some difficulties for the proper acquisition of NMR signal: their structure and the magnetic field inhomogeneities due to the variability of composition and nature (presence of numerous ions, iron content, magnetic susceptibility, grain size) [2], for instance. Nevertheless, NMR methods allow to access to precious information like water content and water in pore size distribution in the range of few nm to mm.

With our proton NMR apparatus we can determine spatially resolved soil water content (imaging), or estimate water distribution in soil microstructure, i.e. as a function of pore size (relaxometry). These two properties are important to characterize a soil structure and to understand and model processes like flow water and colloid mobilization and transfer.

We developed NMR methodologies that allow:

1- to obtain distributions of relaxation times (T_1 and T_2) associated to pore size repartition (biphasic fast exchange model [3]).

2- to measure water content profiles, distinguishing water contained into large pores from water contained into the whole porosity using two different imaging sequences (spin echo and single point imaging).

These methods were applied to about fifty samples of the same soil that was beforehand sieved down to aggregates of three different granulometry, then repacked at various apparent densities and equilibrated to various water content.

To associate T_1 and T_2 measurements offer similar time distributions with essentially four peaks. The two shortest times are associated to pores of the texture, and the two longest times are associated to pores of structure and granulometry. At last, we compared water profiles measured with sequence SPI with water content of sample and we identify water profile measured with spin echo sequence with water in the two longest times associated to structure and granulometry.

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O34 Water Flow Investigation on Quartz Sand with 13-Interval Stimulated Echo Multi Slice Imaging

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Understanding root water uptake in soils is of high importance for securing nutrition in the context of climate change and linked phenomena like stronger varying weather conditions (draught, strong rain). One step to understand how root water uptake occurs is the knowledge of the water flow in soil towards plant roots. Magnetic Resonance Imaging (MRI) is potentially the most powerful analytical tool for non-invasive three dimensional visualization of flow and transport in porous media [1]. Numerous attempts have been made to measure local velocity in porous media by combining phase encoding of the velocity with fast imaging methods [2-4], where flow velocities in the vascular bundles of plant stems were investigated. Since their cells impose almost no limitation to flow, their MR signal is hardly inferred by internal field gradients. The situation in the surrounding soil, a natural porous medium, is different, since there internal magnetic field gradients are not negligible. In this work we account for the existence of these gradients by employing bipolar pulsed field magnetic gradients [5]

for velocity encoding. This enables one to study flow through sand (as a model system for soil) at flow rates relevant for the water uptake of plant roots.

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O35 Determination of Soil Hydraulic Properties Using Magnetic Resonance Techniques and Classical Soil Physics Measurements

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Water and solute movement as any other transport processes through soil are influenced by the hydraulic properties of the soils. The heterogeneities of the soils imply heterogeneous spatial distribution of the hydraulic properties leading to heterogeneous distribution of soil water content. This may affects the water availability for plant growth, the groundwater contamination and nutrients losses within the root zone. The measurement techniques available today for the estimation of soil hydraulic parameters do not account for the heterogeneity of the sample and treat each measurement sample as a homogeneous representative volume. On the other side natural soils contain large heterogeneities mostly in terms of inclusions of different materials. Therefore the purpose of this study is to estimate soil hydraulic properties of a heterogeneous sample by combining classical multi-step-outflow (MSO) with magnetic resonance imaging (MRI) experiments. MSO experiments were performed on a sample filled with sand and sand-clay mixture in a coaxial structure. During each pressure application MRI images at $4.7\,\text{T}$ ($200\,\text{MHz}$) were recorded using a pure phase-encoding MRI sequence in order to provide information about the soil water content at specific locations within the coaxial sample. The recorded cumulative outflow and water content data were used as input data in the inversion of the MSO experiment. For the simulation and inversion of the MSO experiment we used the hydrological model HYDRUS-2D3D in which the initial hydraulic properties of the two materials were estimated based on T_2 relaxation measurements on homogeneous sub-samples. The results show conclusively that the combination of the two MRI and MSO methods leads to a unique estimation of the hydraulic

properties of two materials simultaneously.

4.9 Porous Media in Renewable Resources and Food Science

O36 **Pulsed-Gradient Spin-Echo Monitoring of Restricted Diffusion in Multilayered Structures**

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A general mathematical basis is developed for computation of the pulsed-gradient spin-echo signal attenuated due to restricted diffusion in multilayered structures (e.g., multiple slabs, cylindrical or spherical shells). Individual layers are characterized by (different) diffusion coefficients and relaxation times, while boundaries between adjacent layers are characterized by (different) permeabilities. Arbitrary temporal profile of the applied magnetic field can be incorporated. The signal is represented in a compact matrix form and the explicit analytical formulas for the elements of the underlying matrices are derived. The implemented algorithm is faster and much more accurate than classical techniques such as Monte Carlo simulations or numerical resolutions of the Bloch-Torrey equation. The algorithm can be applied for studying restricted diffusion in biological systems which exhibit a multilayered structure such as composite tissues, axons and living cells.

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O37 **The Effect of Thermal Modification on Microstructure of Wood: PGSTE NMR, Remote Detection MRI and NMR Cryoporometry Studies**

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Thermal modification is a pro-environmental method for increasing the lifetime and properties of timber products [1]. The modification improves the dimensional stability of wood and increases its resistance to biodegradation and weather. In this work, we investigate the changes in microstructure of Pinus Sylvestris pine wood caused by thermal modification using sophisticated NMR techniques. Box-like, long and narrow longitudinal tracheid cells constitute the major part of the wood volume. The hollow interior of tracheid cells is called lumen. We investigate the changes in the lumen dimensions by PGSTE NMR of a fluid absorbed in the lumens. We have demonstrated that, when both gases and liquids are used as probe fluids, the scale of dimensions observable

by PGSTE NMR is over four orders of magnitude, covering all the interesting length scales in the wood cell structures [2]. The experiments show that thermal modification decreases the lumen dimensions in all the three orthogonal dimensions. In addition, the results imply that the wood cell wall structure begins to be destroyed above a critical modification temperature [3]. The lumens of adjacent tracheid cells are connected by tiny pits, allowing water and nutrients to travel between the cells. We investigate the effect of thermal modification on permeability of wood by remote detection MRI [4]. Time-of-flight images of hyperpolarized xenon gas flowing through wood samples reveal that a large amount of the pits are closed in thermal modification [5]. Wood cell walls contain small pores in between microfibrils, whose size is on the order of nanometers. We investigate the size distribution and amount of the nanopores by NMR cryoporometry [6]. Preliminary results imply that a major part of the nanopores are closed in thermal modification, preventing the swelling of wood when exposed to moisture.

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5 Poster

5.1 Connected Porous Systems and Multidimensional NMR Approaches

P1 A T_2D TDNMR Study of Skin

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T_2D TDNMR data is used to improve the assignment of the location of water in in-vitro pig skin. Whilst it is not possible to resolve or uniquely assign water environments in either 1-dimensional T_2 or D data, the T_2D method clearly resolves the data into two components, considered intra- and extra-cellular water.

T_2D data are presented for whole defatted skin, a dermatomed slice of the top $0.4\,$mm (mostly epidermis) and the remaining sub layer (dermis). The assignment of intra- and extra-cellular water is made by considering the peak intensities in the T_2D data from the whole and dermatomed skin sections.

The relative proportion of fast relaxing/fast diffusing water is largest in the epidermis section (which has a close packed cellular structure) so this peak is assigned as intra-cellular water. Whilst there is more slowly relaxing/slowly diffusing water in the dermis section (which has fewer cells within a collagen network) so this is assigned as extra-cellular water. The observation that intra-cellular water is relaxing fastest, suggests that the skin cells contain more exchangeable species, through which the water can relax, than the extra-cellular network.

The resolution between intra-cellular and extra-cellular water is lost on repeated freezing (breaking the cell walls) and also on increasing the diffusion time from 50 to 100 and $150\,$ms, this is likely partly due to relaxation but also due to diffusion through the cell membranes during the experiment. This gives a measure of the cell wall permeability.

P2 Structure of the Two-Dimensional NMR Relaxation Spectra of Porous Materials

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Two-dimensional NMR-relaxation spectroscopy, correlating various relaxation mechanisms, proved useful for studies dynamical processes that take place in various porous material [1-5]. Yet development of the Laplace-spectroscopy has

been somewhat impeded by difficulties in creating a stable numerical multidimensional Laplace-inversion method free of faulty premises. Herein we shall discuss in terms of the eigenmodes theory a number of fundamental structural properties, viz. symmetries, overall intensities, signs and relative intensities of the diagonal and cross components, of the two-dimensional NMR relaxation spectra which could be used as constraints to design a stable and fast Laplace-inversion algorithm.

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$\boxed{\text{P3}}$ Solid-State ^{1}H and ^{13}C MAS NMR Investigations of European Coals

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In this study, the results of solid-state NMR (SSNMR) investigations of two sets of European coals (from Germany and the Czech Republic) are summarized. We have performed solid-state ^{1}H and ^{13}C magic angle spinning (MAS) NMR as well as [1]H–[13]C heteronuclear correlation (HETCOR) experiments on these coal samples to determine their structures. Rank of these coals was obtained by straightforward ^{13}C one dimensional cross polarization (CP) with MAS NMR experiments and compared with results from the petrographical analysis; the results from both experiments are in well agreement. The carbon aromaticity (protonated, alkylated, phenolic or condensed) and the ratio between ternary and quaternary aromatic carbons were classified, for example by [1]H-^{13}C HETCOR experiments. In addition, solid-state ^{1}H MAS NMR results obtained with very high spinning rates are presented. This leads to the conclusion that SSNMR is a powerful method to determine the structural features of coal. Finally, the interactions between probing gases including CO_2 and Xe and porous coal samples were studied using ^{13}C and hyperpolarized [129]Xe NMR spectroscopy. The preliminary NMR results of CO_2 and Xe adsorption in coal samples will be presented.

P4 | [1]H T_2–T_2 Exchange Measurements in Low Field NMR

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The nuclear spin relaxation of a fluid enclosed within a porous material is modified by the diffusion between different regions and collisions with the pore surfaces due to stronger magnetic dipole-dipole interactions and the presence of paramagnetic impurities present in the walls. The relationship between the transverse relaxation times in fluids imbibed in porous media and the pore size, morphology and S/V distributions and can be divided in two regimes known as fast and slow exchange, which is associated with the fluid dynamics inside such materials. Multidimensional low field NMR has become a very important technique to investigate fluid dynamics enclosed in porous media such as oil reservoir rock cores. The T_2–T_2 exchange experiment, published by Jing-Huei Lee (1993), is a combination of two CPMG like pulse trains separated by a mixing time, which allows identifying the transition of spins within different transverse relaxation time regions, which is potentially useful for porous media permeability determination. Whether used for soft matter applications (e.g., exchange between liquid crystal domains), in biophysics (exchange of metabolites between the interior and exterior of cells) or in porous media studies (migration between pores), the ability to quantify details of exchange between specific subpopulations could prove of significant value. This work shows [1]H T_2–T_2 exchange measurements for a set of different water saturated rock cores. They were measured using a Kea2- Magritek spectrometer equipped with a 12-MHz Halbach array and the data set was processed trough a 2D inverse Laplace transform developed in the Victoria University of Wellington. The fluid dynamics inside these porous mediums was observed by taking the T_2–T_2 maps for a set of different mixing times, where each map represents a snapshot of the evolution of the system between two sequential states, and comparing the intensities of the peaks within and off the diagonal. The results show the capability of doing this kind of measurements on much lower sensibility spectrometer (12-MHz magnet) as compared to the systems already described in the literature.

P5 Hydrology Studies of Heap Leaching Columns Using Magnetic Resonance Imaging

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In recent decades heap bioleaching has become a widely applied method for the recovery of valuable metals such as copper from low grade ores. In this process iron and/or sulfur oxidising microorganisms that are present in the ore heaps are used to facilitate the oxidation of base metal sulfides, thereby liberating the metal ions into solution. Accordingly, one of the main challenges in the optimisation of this process is the heap hydrology. Heaps are unsaturated systems of often highly inhomogeneous nature which makes their hydrology complex and spatially variable. This often leads to issues such as flooding and preferential flow which ultimately effects the metal recovery. Though many hydrology studies have been done on this topic, most of them have adopted a "black-box" approach. Some studies have used x-ray computed tomography [1], but this cannot be used during an experiment as x-rays can sterilise the system. Thus none of the current methods allow for the real time imaging and analysis of the leaching systems. The application of magnetic resonance imaging (MRI) to heap leach systems can bridge this gap by non-invasively imaging a column acid leach. Spin-echo acquisition methods were found to be inappropriate for imaging the ore as the copper, iron and other paramagnetic species in the ore caused significant magnetic susceptibility distortions. Single Point Imaging (SPI) though was shown to be able to image the ore with minimal artefact formation. SPI is a relatively inefficient imaging method and the long acquisition times often force compromises in the number of scans, so limiting the signal to noise ratio (SNR). In order to counteract this, multiple point acquisition (MPA) was employed. This allowed for improvements in the SNR without any increases in the acquisition times. T_2^* mapping was performed as an extension of this, the results of which allowed for the construction of proton maps which were free of any T_2^* weighting.

The presented study is an abiotic leach of copper ore packed in a $50\,\mathrm{mm}$ diameter column where the ore bed was imaged at different stages during the leach. The acquired 3D images were used to evaluate the bed structure and porosity as wells as the solution and gas distributions. The results were compared to standard "black box" type measurements [2] to determine their accuracy and were found to be in agreement. The images also allowed for the correlation of flowing solution position with the surrounding bed structure.

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P6 Drying of Starch, Gelatin and Paint: A Comparative Study

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Starch, well known as a porous biopolymer, was investigated during its film formation. 5% and 1% starch in D_2O (w/v) were gelatinized to make a homogeneous suspension and cast for the preparation of film. Real-time drying was studied using low-field ($0.27\,T$) single-sided Nuclear Magnetic Resonance (NMR) with a depth resolution of $50\,\mu m$. Spin-spin relaxation times (T_2), measured at different layers, reveal that molecular dynamics involved during the film formation of these samples are different. It was also found that the starch film formation process is not homogeneous. The final films were characterized using NMR, X-ray diffractometry (XRD) and Differential Scanning Calorimetry (DSC). The results obtained from the above single-sided NMR study were compared with that of 10% gelatin in D_2O (w/v) solution system evaporation and two types of epoxy paint (solvent-rich and solvent-free) coatings study. It was observed that the gelatin system under investigation dried faster from the bottom of the sample [1] while the paint dried faster from the air-sample interface [2].

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P7 Real-Time Investigation of the Film Formation of Gelatin Biopolymer Using Single-Sided Low-Field NMR Relaxometry

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Gelatin solutions of different concentrations were prepared in D_2O (w/v). Single-sided Nuclear Magnetic Resonance (NMR) scanner was employed to follow the drying process of the cast solution until film formation. The NMR scanner having a low-field ($0.27\,T$) and a strong static magnetic field gradient ($490\,kHz/mm$) was used for the determination of spin-spin relaxation times (T_2) at different layers with microscopic resolution. The macroscopic evolution of the gelatin solution was also observed optically from the reduction of the sample thickness which reveals that at the macroscopic level, the process is not uniform throughout the experiment. From the NMR results it is observed that the gel appears to be drier in the upper layers near the evaporation front at early stage, while this tendency is inverted at the later stages, when drying is faster from the bottom [1]. The final films were characterized using NMR and X-ray diffractometry (XRD) to verify the drying behavior [2].

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P8 Effect of Crystallization Inhibitors on Drying Behavior of Porous Building Materials

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While the mechanisms of salt damage in porous materials have received considerable attention in recent years, effective treatment methods for ameliorating this common problem still remain limited. The use of salt crystallization inhibitors has been suggested in the past. However with mixed results and as such the suitability of these materials for the treatment of salt damage is still under discussion. Recognizing the need for further information regarding the function of crystallization inhibitors in salt contaminated porous media, their effect on the drying behavior of salinated porous materials has been studied. Drying experiments using potassium hexacyanoferrate (II) trihydrate inhibitor dissolved in 3 m NaCl solution were performed, and monitored using nuclear magnetic resonance spectroscopy (NMR).

Droplets (300 μl) of NaCl solution containing different concentrations of crystallization inhibitors were dried on a Polymethyl methacrylate (PMMA) substrate under controlled conditions. Direct imaging of the drying droplet was achieved using a digital microscope to record the onset of crystallization and the crystal morphology. NMR measurements were performed simultaneously to record the solution concentration in the droplet during drying. The results show a delay in crystallization (super-saturation), growth inhibition and a change in crystal morphology in the presence of inhibitor.

Further drying experiments were also performed using brick substrates to determine the effect of the crystallization inhibitor within a porous material. Fired clay bricks saturated with 3 m NaCl solution containing different concentrations of inhibitors (0.001 m, 0.01 m and 0.1 m) were dried under controlled conditions. Preliminary results show a faster drying rate and higher super-saturation prior to the onset of crystallization for samples containing an inhibitor. The formation of abundant efflorescence and alterations in crystal morphology were also observed. The influence of inhibitor concentration on the drying rate was also assessed.

P9 Two dimensional Exchange Experiments of Natural Porous Media with Portable Halbach-Magnets

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Mobile NMR has its origin in well-logging. By now there are numerous applications of mobile NMR in materials analysis and chemical engineering where, for example, unique information about the structure, morphology and dynamics of matter is obtained, and new opportunities are provided for geo-physical investigations [1]. In particular, dynamic information can be retrieved by two-dimensional Laplace exchange NMR, where the initial NMR relaxation environment is correlated with the final relaxation environment of molecules migrating from one environment to the other within a so-called NMR mixing time t_{m} [2]. Relaxation-relaxation exchange experiments were performed with saturated and un-saturated soil samples at low and moderately inhomogeneous magnetic field with a simple, homemade, portable Halbach-Magnet. By executing such exchange experiments for several mixing times and inverting the results to 2D T_2 distributions (reminiscent of joint probability densities of transverse relaxation times T_2) with the help of the inverse 2D Laplace Transformation (ILT), we observed characteristic exchange processes under saturated conditions: soils consisting mainly of silt and clay components show predominantly exchange between the smaller pores at mixing times of some milliseconds. There exists also weaker exchange with the larger pores observable for longer mixing time. In contrast to that fine sand exhibits 2D T_2 distributions with no exchange processes which can be interpreted that water molecules move within pores of the same size class [3]. For the first time we compared these results with the exchange behaviour at different saturation levels. For fine sand the relaxation times only shifted to faster values and no additional exchange process appeared. As opposed to that for soil samples the slow relaxation processes vanished whereas the fast processes remain constant. So we conclude that the drying process in fine sand results in the formation of water films on the surface of the solid. The more heterogeneous soil samples lost predominantly the water from the larger pores and show an exchange dynamic between the smaller pores up to low water contents.

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P10 Feasibility Study of NMR and X-Ray CT Based Pore Space Characterisation of Drill Cuttings

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Deep underground reservoirs of oil, gas or hot water are usually located and explored by applying surface geophysics (e.g. seismics) followed by drilling a well at the most interesting location. Usually drill cores are extracted from the reservoir strata for further laboratory studies aiming at the estimation of pore space characteristics such as porosity and permeability. Since the extraction of drill cores is very cost-intensive it would be worthwhile to get the relevant petrophysical parameters from measurements on drill cuttings, which are a by-product of almost every deep drilling process. So we are focusing on petrophysical studies on drill cuttings. Our samples originate from a deep geothermal drilling project in the city of Hanover, Germany. Besides petrophysical standard methods, low field ^{1}H NMR relaxometry measurements to determine pore size distributions and micro CT measurements to visualize pore space were performed. Both methods complement each other, since NMR captures an assemblage of cuttings from a certain depth and CT allows a high resoluted view into single cuttings. Furthermore ferreous minerals, which also influence NMR measurements, can be easily pinpointed by CT. In general, drill cuttings are a very challenging porous material for low field NMR relaxometry because they are tiny and the successful exclusion of water adhering to the outer surface is strongly dependent on sample preparation. Nevertheless it was possible to distinguish between different pore space characteristics of drill cuttings obtained from different depths.

P11 Freezing and Melting Behaviour of Fluids in Random Mesopores

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Fluids confined to mesopores often exhibit a rich variety of phenomena not typical for bulk substances. Among them, hysteretic melting-freezing phase transitions have attracted particular attention and have been thoroughly studied. However, some aspects of these phenomena are still subject of experimental and theoretical studies [1].

In this contribution, we report on freezing and melting behavior of nitrobenzene confined to pores of Vycor porous glass as revealed by nuclear magnetic resonance cryoporometry [2]. The two transitions are found to exhibit a broad hysteresis loop, typical for liquids in mesoporous solids with random pore structure. To get deeper insight into the particular mechanisms leading to the hysteresis observed, scanning experiments exploiting temperature reversal upon incomplete freezing or melting have been performed. Notably, such scanning experiments have frequently been used in the context of sorption hysteresis [3] but rarely of freezing/melting one [4].

The experiments performed in this way clearly show that different cooling and warming histories result in different solid-liquid configurations within the pore system. Further evolution of the thus attained configurations with changing temperature unveiled important information about the transition paths. In particular, these experiments indicated the occurrence of a pronounced pore-blocking for freezing, resulting in a temperature-delayed freezing transition via invasion-percolation [5]. The melting, on the other hand, is found to occur homogeneously over the whole pore network and to resemble properties typical of the equilibrium transition.

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P12 Pulsed NMR Measurements of the Water Adsorption on Chitosan Samples Dried in Different Conditions

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Interrelation between a structure and adsorption of water vapors on chitosan samples is studied. Pulsed NMR experiments, IR spectroscopy and X-ray diffraction showed an influence of preliminary treatment as freeze-drying after precipitation with NaOH or Na_2CO_3 or drying in air as well on chitosan supramolecular structure. The freeze-dried chitosan samples have a more ordered structure compared with that dried in air. Porous structure parameters of the chitosan samples calculated from both water vapors at 293 K and nitrogen vapors at 77 K adsorption isotherms were compared with pulsed NMR data. The combined analysis of both free induction decay (FID) signals and spin-echo decays obtained in the CPMG experiment allow to analysis getting a complete set of spin-spin relaxation times. Self-diffusion coefficients of water molecules adsorbed on the chitosan samples were measured by NMR PMFG method with the maximum PMFG value of 60 T/m. The pore sizes distribution in the freeze-dried chitosan samples where water molecules are adsorbed

determines an existence of a set of self-diffusion coefficients of adsorbed water. The loose macromolecular packing of the chitosan cryogel is adequate to the mesoporous structure with a larger volume accessible for water compared with the air-dried sample. The increase of water adsorption leads to increasing relative fraction of water in the largest mesopores from 2 to 42 %. The performed pulsed nmr experiments on measuring of spin-spin relaxation parameters and self-diffusion point to the differences both in the arrangement of chitosan macromolecules (ordered or disordered supramolecular structure with different packing of chains) in the samples dried in different conditions and mobility of water molecules adsorbed on chitosan, as well. The results obtained agree with the results of X-ray diffraction and IR-spectroscopy investigations.

P13 NMR Diffusion Correlation and Exchange Spectroscopy in Inhomogeneous Fields

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Diffusion sensitive NMR techniques have proven to be particularly useful to study molecular transport phenomena of liquids in porous media. Among them, two-dimensional correlation experiments can be used to study exchange processes in systems that exhibit various diffusion coefficients reflecting different local environments. In combination with 2D Inverse Laplace Transformation two-dimensional diffusion spectra can be obtained where exchange processes show up in off-diagonal peaks.

We have performed two-dimensional diffusion correlation experiments in presence of the strong constant magnetic field gradient of a single sided NMR spectrometer with a proton Larmor frequency of 11.7 MHz. A sequence based on stimulated spin echoes was used in which the relevant diffusion time as well as the setting of different mixing times is possible. We have developed a phase cycle in order to suppress unwanted coherence pathways beside the desired one.

With this technique we studied the diffusion and exchange properties of organic solvents in a packing of commercial zeolite crystals. For the analysis we used 2D Inverse Laplace Transformation as well as time domain fitting to observe the exchange process at various mixing times. In addition the time-dependent exchange patterns of the self-diffusion coefficient distributions are compared to simulated data.

P14 How to Quantify Spatial Ordering of Permeable Membranes Using Time-Dependent Diffusion MR

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Diffusion-weighted NMR is used to characterize microstructure of materials, porous media, and biological tissues. The universal signatures of restrictions to

molecular motion, such as the surface-to-volume ratio S/V of barriers (membranes), can be determined using the short-time limit of the diffusion coefficient $D(t)$ [1]. Recently, the membrane permeability and the ratio S/V were related to the full $D(t)$ dependence assuming completely uncorrelated flat membranes in any spatial dimension [2]. In general, the time-dependence of $D(t)$ depends in a non-universal and complex way on the geometry of the restrictions.

What can one infer about the packing geometry (ordering) of permeable membranes from a measured $D(t)$? The relation between $D(t)$ and microstructure is a notoriously unresolved problem. Here we address it in one dimension. We show that the form of the probability distribution function (pdf) $p(a)$ of the intervals $a_m = x_m + 1 - x_m$ between successive positions x_m of membranes crucially affects the long-time limit of $D(t)$.

We focus on the way $D(t)$ approaches the tortuosity asymptote D_{tort}. We derive the exact long-time asymptotic behavior $D(t) - D_{\text{tort}} = C[p]/\sqrt{t}$ and relate it to the pdf $p(a)$ of the intervals between the membranes.

As a result we find that $C[p]$ is solely determined by the first two cumulants, the mean and variance, of the pdf $p(a)$. In particular, $C[p]$ is proportional to the variance of $p(a)$. Hence, remarkably, the long-time asymptotic limit of $D(t)$ is insensitive to the shape of $p(a)$ as long as its variance exists; for instance, both the Poissonian and the lognormal pdfs with equal variance indeed yield the same $D(t)$ asymptote, as we verify with Monte Carlo simulations of one-dimensional diffusion restricted by the membranes distributed according to different pdfs $p(a)$.

The shape of $D(t)$ changes qualitatively when the variance of $p(a)$ vanishes. In this limit, the way the tortuosity limit is approached switches to $D(t) - D_{\text{tort}} \sim 1/t$, in agreement with earlier results for a periodic system [3]. When the variance diverges, which occurs when the pdf $p(a) \sim 1/a^\nu$ has a »fat tail« (i.e. is of a Levy form), the asymptotic power-law behavior $D(t) - D_{\text{tort}} \sim t^{-z}$ allows one to determine the power $\nu = 1 + 2z$ of the Levy-stable pdf of intervals.

Conclusions: The leading inverse-square-root time dependence, a defining signature of permeable membranes [2], is quantitatively related to how randomly the membranes are distributed in space. Measuring the prefactor $C[p]$ in the long-time asymptote of $D(t)$ can thus allow one to quantify the degree of structural irregularity of a sample.

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P15 Imaging of Water and Water Vapor Uptake in Thin Nylon Films

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The variety of applications of nylons (or polyamides) leads to the interest to study fluid uptake processes. Either used as an engineering plastic, high strength fiber or packaging material, fluid uptake will affect the properties of nylon. For a better understanding the fluid uptake process is studied using NMR imaging. The NMR is used to obtain several types of information. Primarily the NMR is used to measure the water distribution during the process of water uptake or drying of the films. Secondarily material properties are available in the form of the signal decay providing information about the rigidity of the polymer matrix and the state of water in this matrix. The goal of the presented study is to understand the sorption process at room temperature by quantification of the NMR signal.

The water distribution in a thin film ($200\,\mu$m) is imaged using the GARField approach [1]. Specially shaped poles give a gradient of $43\,$T/m. This setup can obtain profiles with a resolution of about $6\,\mu$m. The NMR setup is modified with a climate chamber. This chamber allows control over the temperature and relative humidity (RH) during measurements. A desired RH is created by mixing water and air in the right ratio and injecting it into the chamber. Our climate chamber in combination with a stimulated echo pulse sequence gives directly access to the diffusion coefficient as opposed to the indirect methods found in literature [2,3].

The NMR signal profiles are obtained while liquid water is placed on top of a nylon film. The obtained NMR signal is due to two species of hydrogen: one attached to the polymer and the other one coming from the water penetrating the polymer film. Experiments with heavy water (D_2O) revealed the plasticizing effect of water on the nylon. To gain further insight in the effect of water or water vapor on the plasticization additional techniques such as DSC and DMTA are employed. To quantify the NMR signal in terms of water contents a sorption isotherm has been measured with gravimetry and with NMR.

The measurements show a front penetrating the film and at approximately five hours this front reaches the bottom of the film. At this moment a concentration gradient is shown from the top to the bottom of the film. The motion of the waterfront is non-Fickian, different from observations at high temperature [2]. During the next ten hours the film is homogeneously filled with water. The measurements also reveal a slower process, observed as a signal increase throughout the whole depth of the film, related to plasticization of the polymer matrix.

A unique study combining NMR experiments and gravimetric experiments provides the means to give a quantitative view of the water uptake of a nylon film at room temperature. Non-Fickian uptake behavior and slow polymeric

rearrangements have been observed.

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P16 **Dynamic Correlations Between Susceptibility Gradients and T_2-Relaxation as a Probe for Wettability Properties of Liquid Saturated Rock Cores**

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The dynamic behavior (relaxation and diffusion) of the NMR signals from liquids confined in rock core samples is sensitive to surface interactions and can potentially be used for characterization of wettability properties [1]. The T_2 distributions of water and oil do however often overlap. Diffusion-T_2 (D–T_2) correlation measurements can be used for separating oil and water signals, thus increasing the resolution of the measurement [2]. We however explored the use of correlations between susceptibility gradients and T_2-relaxation (G_0–T_2) [3,4], and showed how the difference in response for oil and water with respect to G_0 can potentially be used for improved characterization of wettability. We compare the use of G_0–T_2 correlations to measurements of D–T_2 correlations.

The measurements were performed at 35 °C on a Maran DRX 12 MHz spectrometer (maximum gradient strength of 225 Gauss/cm). The sample studied was a water-wet Berea sandstone rock core. G_0–T_2, and D–T_2 measurements were compared in water-saturated (S_w) and irreducible water saturated (S_{wi}) states. To reach the S_{wi} state synthetic oil (Marcol82, Exxon Mobile) was flooded through the rock core.

D–T_2 correlations were measured using a combined PGSE-CPMG sequence [5]. G_0–T_2 correlations were measured using a modified CPMG sequence suggested by Sun and Dunn [3], where G_0 is not measured directly, but through DG_0^2. The data were analyzed using 2D Inverse Laplace Transformations.

The D–T_2 correlations in the S_w state revealed a narrow distribution of diffusivities for water around 2.3×10^{-5} cm^2/s. Unfortunately, for D–T_2 correlations in the S_{wi} state all signals from water were lost due to strong influence from diffusion in susceptibility gradients during the PGSE-part of the sequence. The mean diffusivity for the remaining oil signal was 6.10×10^{-7} cm^2/s.

The DG_0^2–T_2 correlations in the S_w state showed a broad distribution of G_0 in the range 10–200 Gauss/cm. For DG_0^2–T_2 correlations in the S_{wi} state, the signals from oil and water were totally separated along the DG_0^2-dimension. In contrast to the D–T_2 correlations, signal from water still remained. When normalized with respect to the measured diffusion coefficients, G_0 for the two water peaks were 50 and 200 Gauss/cm, and for the oil peak 30 Gauss/cm.

We found that the dynamic range along the DG_0^2 dimension was larger than

the range along the corresponding D- or T_2-dimensions, potentially making this dimension more sensitive to changes in wettability.

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$\boxed{\text{P17}}$ 2-D Relaxation and Diffusion Measurements of Biofouled Porous Media

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2-D relaxation correlation experiments including T_1–T_2, T_2–T_2, D–T_2 and D–T_1 measurements have been used to probe pore size distributions and surface characteristics of porous media [1-4]. This study uses these techniques to verify the growth of a biofilm throughout a porous medium. The bacteria chosen, Bacillus mojavensis, has shown resistance to super-critical carbon dioxide, and the non-invasive detection of biofilm growth may have applications for carbon sequestration and storage. Initial measurements using model bead packs showed a change in relaxation behavior based on the degree of biofouling of the sample. This study uses a number of Berea sandstone rock core samples. Each rock was initially characterized by saturation with both a brine solution and the bacterial growth media solution. A biofilm was then grown throughout the pores of the rock with a pressure-driven flow. 2-D relaxation measurements showing the changes in the pore structure and surface environments due to the growth of the biofilm, primarily due to the hydrogel produced by the bacteria occupying the pores, were used to establish the presence of biofilm within the rock.

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P18 MRI Analysis of the Interactions Between Moisture Transfers and Hydration Occurring During the Repair Procedure of an Aging Concrete

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The degradation of a reinforced concrete structure by corrosion of steel bars is a major economic problem nowadays. In order to extend the service lifetime of degraded concrete structures and their future integrities by preventing the deterioration of degradation, it is generally recommended to repair and to rehabilitate the cracked and/or carbonated concrete surface.

However, existing repair techniques are generally based on empiricism. In particular, the performance of the repair process is jeopardized by moisture transfers occurring at interfaces between dry aging concrete and wet repair mortars, due to the fact that the desiccation of early-age mortar could slow down its hydration and hinder the setting. This work focus on two points: the quantification of moisture transfers and their impacts on hydration of repair mortar, and the apparition of a coarser microstructure and cracks due to shrinkage. The disorders which impair the durability are analyzed through different techniques. Magnetic Resonance Imaging (MRI) is a non-destructive technique which tends to be developed in civil engineering. Despite of intrinsic difficulties related to heterogeneous microstructure of cement-based materials and to presence of iron, MRI provides reliable and reproducible measurements. Our device also allows us to study proton NMR, thus to quantify free water during the process from mixing to hardening and to analyze the evolution of microstructure (By monitoring of longitudinal relaxation time T_1).

Several mortars that are made of grey cement, which possibly contains admixtures like mineral additions, lightweight aggregates, super-absorbent polymers, aramid fibers, etc., have been studied. They correspond to usual mixed designs for repair work which are particularly characterized at a low water-to-cement ratio (0.3–0.4) so as to limit moisture transfers and the risk of drying shrinkage, to promote self-desiccation, and to obtain a quick setting to enable an excellent adherence.

By NMR, the setting and hardening time have been firstly characterized for various repair mortars which are isolated from the surrounding environment. The rate of endogenous free water consumption has been monitored and we find that perfectly correlates to evolution of heat released during hydration, whereas the setting time determined by the penetration depth of Vicat needle occurs later. The consumption of free water measured by NMR agrees with the computed values obtained by a hydration model. By MRI, the water evolution has been followed for 1D configuration from the repair mortar to aging concrete and surrounding environment. Furthermore, traditional techniques such as gamma-ray attenuation have also been used to validate the MRI measurements. As a

result, moisture transfers for different repair mortars, as well as their impact on microstructure (porosity and pore size distribution) have been evaluated.

P19 Anisotropic Self-Diffusion of CO_2 and CH_4 in the Microporous Imidazolate MOF IMOF-1

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Self-diffusion studies of CO_2 and CH_4 adsorbed in the recently introduced microporous metal-organic framework IMOF-1 [1] were performed by pulsed field gradient nuclear magnetic resonance (PFG NMR) [2] in the temperature range of 203 K to 338 K. The metal-organic framework IMOF-1 belongs to the zeolitic imidazole frameworks (ZIFs) [3], in which tetrahedral coordinated metal atoms (here: zinc) are linked through nitrogen atoms by ditopic imidazolate linkers (here: Imidazolate-4,5-dicarboxylate) to form neutral frameworks. In the case of IMOF-1 the framework consists of one dimensional hexagonal channels with a pore diameter of 0.38 nm. For such a one dimensional pore structure we expect anisotropic diffusion behaviour, with one self-diffusion component parallel and one perpendicular to the channels, described by a model of Callaghan et al. [4]. For CO_2 we found a strictly one dimensional diffusion behaviour along the channels ($D_{para} = 2.5 \times 10^{-9}\,m^2/s$ at room temperature). In contrast, the studies of CH_4 adsorbed in IMOF-1 show also a self-diffusion component perpendicular to the channels. However, the mobility perpendicular to the channels is three orders of magnitudes slower then parallel to the channels ($D_{para} = 4.3 \times 10^{-9}\,m^2/s$, $D_{per} = 8.3 \times 10^{-12}\,m^2/s$ at room temperature). The diffusion from one channel to the other might be effected by small defects in the crystal structure, which are not present in the sample loaded with CO_2. Although the kinetic diameter of both adsorbate molecules, are comparable with the pore diameter in the IMOF-1, the observation time dependent PFG NMR data do not show evidence for single-file diffusion. The obtained temperature dependent self-diffusion coefficients were analysed using an Arrhenius approach. Activation energies of CO_2 adsorbed in IMOF-1 are at 6 kJ/mol and higher values are obtained for methane ($10 \pm 2\,kJ/mol$).

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5.2 Micro- and Nanostructured Materials

P20 **Rheo-NMR Investigations on Polymer Melts and Polymer Clay Nanocomposite**

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Rheo NMR is widely used for the investigation of rheological properties of complex fluids [1-3]. The determination of the flow pattern from the combination of NMR imaging and PFG NMR yields spatially resolved rheological information and shows phenomena like wall slip directly. Velocity maps in combination with measurements of other NMR parameters under shear provide versatile information into molecular properties like orientation and local dynamic depending on flow. The flow properties of polymer melts are of great interest both for fundamental research and technical application. There are numerous NMR investigations of polymer melts but no in situ measurements of polymers in molten state under shear so far. Rheo-NMR is only applied under ambient temperatures so far, for molten polymers a rheo-NMR equipment exceeding temperatures of 220 °C is required. A special, in-house built probehead, fitting in a 300 MHz WB magnet with a micro2.5 gradient equipment accepting a 10 mm Couette cell has been used. The sample is heated by hot air and a special cooling and control system prevent damage of the cryo magnet. We utilized this high temperature rheo-NMR system with a Couette cell for NMR investigations of melts of poly(propylene) and poly(propylene)/clay nanocomposites at steady flow. The influence of different temperatures and shear rates on chain mobility and ordering is demonstrated by means of relaxation measurements and DQ experiments. The velocity profile is derived by a combination of imaging and PFG NMR. Increased mobility in the melt is found in reduced residual dipolar couplings and longer transverse relaxation times. Partial orientation under shear counteracts these.

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P21 Following a Low-Mobility/High-Confinement Liquid FID Component During the Hydration of White Portland Cement

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In a recent work [1,2], the evolution of white Portland cement (WPC) based endodontic pastes (MTA, WPC with added $CaCl_2$ and WPC with added NaF) has been studied by Time-Domain ^{1}H-NMR. In particular T_1 and T_2 relaxation time distributions have been used to characterize the evolution of the different pastes. In all the samples, the FIDs showed the formation of at least two pools of ^{1}H nuclei. The two groups were distinguished in the FIDs by fitting each FID to the sum of a quasi-Gaussian and an exponential. The quasi-Gaussian was interpreted as a low mobility ^{1}H group, the so called solid-like component, and the exponential as a high mobility ^{1}H group, the liquid-like component. However, it was clear that the two-component fit was only a robust approximation, because the initial solid-like portions of the FIDs had contributions from more than just one component. In particular, a component, intermediate between solid and liquid, seemed to contribute partly to the solid-like and partly to the liquid-like components.

In this work, we present a more detailed analysis of the FIDs. For FID signals obtained in Inversion-Recovery (I-R) T_1 measurements on White Portland Cement during some weeks of hydration, an attempt has been made to follow in some detail an FID component with exponential decay and T_2 somewhat under a hundred microseconds. This is in addition to at least two solid components, with different forms of Gaussian or modified-Gaussian decay and with time constants well under $20\,\mu s$, in addition to a very much larger liquid signal with FID decay time varying with both I-R time and hydration time. Each FID was fit with three amplitudes, total Solid, Liquid-Short (LS), and Liquid-Long (LL), in order to make files from which to compute T_1 distributions. To do this it was first necessary to determine, as functions of I-R time and for each hydration time, the FID decay rates for the liquids and to determine the quasi-Gaussian rate and two additional shape parameters to represent the quasi-Gaussian decay of the solid contribution to the FID. Fits were made in Psi-Plot to stacks of FIDs to determine these eight parameters at short I-R times. The decay rate for LS showed considerable scatter but appeared not to vary significantly with I-R time and was also about the same for most hydration times, about 13 (1/ms). T_1 for LS is a little over a ms for all I-R times and all hydration times. The LS amplitude varies about linearly with the total Solid amplitude, but with an intercept.

This intermediate Liquid-Short component is a candidate to be interpreted as the signal from water adsorbed in the intra-layer regions of C-S-H gel of the size of a fraction of a nanometer [3].

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P22 A Study of Silver Species on Silver-Exchanged Chabazite, ETS-10 and Mordenite by XRD, SEM and Solid-State ^{109}Ag/^{29}Si/^{27}Al NMR Spectroscopy

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Silver-exchanged zeolites have been utilized in synthesizing antibacterial materials, catalysts and gas separators for inert gases Ar, Kr and Xe [1,2]. These properties arise from different chemical states and positions of silver species on zeolite supports. Classic zeolite is composed of rigid aluminum silicate framework with negative charges and exchangeable cations, the former of which provides an interface for the interaction of cations, in this case, silver ions. Due to different repetitive unit and its arrangement, zeolite structure could be very different, which clearly has control over the chemistry of silver species on zeolite. Upon heating, silver cations in zeolites can form clusters with a wide range of compositions including metallic or charged nanoensembles. The clusters, ions and metallic silver may occupy different sites in zeolite, depending on the thermal activation process. To effectively utilize silver-exchanged zeolites, it is important to understand the change of silver ions to other silver species during thermal activation over various zeolites. In this study, three kinds of silver-exchanged zeolites, Ag/chabazite (Ag/Chab), Ag/ETS-10 and Ag/Mordenite (Ag/Mor) were investigated during thermal treatment under different environments, Ar, air and H_2. Characterization techniques such as XRD, SEM as well as solid-state ^{109}Ag, ^{29}Si and ^{27}Al NMR spectroscopy have been applied to study the silver species formed and the effects of zeolite supports. After treatment in H_2 at 400 °C, silver ions on chabazite and ETS-10 were fully reduced, while silver ions on mordenite mainly remained with few reduced to metallic silver particles. In Ar or air streams at 400 °C, silver ions most remained on mordenite, partly remained on ETS-10, while completely converted to other silver species on Ag/Chab. XRD, SEM and solid-state ^{29}Si and ^{27}Al MAS NMR results indicated that the frameworks of chabazite, ETS-10 and mordenite remained during thermal treatments in Ar and air at 400 °C, but in H_2 at 400 °C, there is a little local structural change for mordenite and a collapse for chabazite and ETS-10. The presence of H_2 at 400 °C barely affected the state of silver ions on mordenite, possibly due to the strong interactions between silver cations and the structural oxygen in mordenite. It is clear that zeolite structure greatly affects the interaction between silver cations and zeolite. It is believed that the interaction between morndenite and silver is the strongest with chabazite and

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P23 Obtaining Pore Size Distribution of Industrial Particulate Filters via the NMR-MOUSE©

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Since mercury intrusion porosimetry (MIP), one of the predominant methods for obtaining pore size distributions, is associated with high costs and nature pollution due to the toxicity of mercury. Therefore another reliable analysis method is needed. Moreover, in the coming years an EU-wide prohibition of mercury will be established limiting even the use of analytical devices. Our goal was to show that the NMR-MOUSE© is capable of obtaining a signature of pore size distributions in a noninvasive way of a small brick sample from an industrial particulate filter (used in automotive scrubber systems) that can be directly related to mercury intrusion porosimetry data.

Under an average field gradient of $20\,\text{T/m}$ the water saturated sample was studied with a CPMG pulse sequence using the NMR MOUSE©. The Inverse Laplace Discrete Transformation (ILDT) of the NMR signal yielded not only the shape of the pore size distribution but also inner structure properties that were unexpected. With the sensitive volume that was fully covered by the thin walls of the filter due to the tunable parameters, it could be shown that the thin layer walls of the porous sample have porosity inhomogeneities. Those can be linked to the manufacturing of this material by extrusion. Bulk porosity and pore size distribution validated by MIP, structural dimensions validated by digital microscopy and the convenience of fast, noninvasive and easy use demonstrate the potential of the NMR-MOUSE© as a mobile and unique analytical tool.

P24 Characterization of Porous Media at 17.6 Tesla - Preliminary Results

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NMR methods are widely used to determine chemical and physical properties of materials. Especially the investigation of micro- and mesoscopic structures have gained increasing interest. A number of different methods have been developed to access these information, e.g. pulsed field gradient or relaxation

methods. These methods are well understood and have been thoroughly studied at low magnetic field strengths. The feasibility of these methods at high fields as well as effects only detectable with very high resolution microscopy are evaluated in the presented study.

While the high field strength promises a high SNR and a possible high spatial resolution it gives also rise to severe problems especially at heterogenous structures such as porous media. At field strengths as high as 17.6 T the internal gradients induced by susceptibility differences inside the porous structure are comparable or even stronger than imaging gradients for microscopy. This is a severe issue when using pulsed gradient methods. Furthermore the connection of the T_2 relaxation time on the surface to volume ratio may be changed by the internal gradients. In order to apply the methods established at low fields, the issue of internal gradients is approached by susceptibility matching and its efficiency is investigated.

In a second step a diffusion relaxation effect is analyzed for its potential to yield information on the microstructure of a layer near the surface of a porous media. The idea is to store information about the porous media in the relaxation of the spins. The self diffusion of the water transports these information outside the porous media where it can be detected. As this layer containing the information around the porous media is thin at applicable diffusion times high resolution images are necessary to quantify this effect.

Using T_1 relaxation experiments it was possible to estimate pore size distributions inside the porous media. As T_1 measurements are less prone to internal gradients than T_2 measurements no susceptibility matching of the probe was necessary. Furthermore, pulsed field gradient experiments can be used even at very high fields as long as internal gradients in the sample are being compensated by the use of susceptibility matching. Without this susceptiblity matching it was impossible to get meaningful results from the measurement.

The diffusion relaxation effect, manifesting itself in a white ring about the porous material, yields signal related to the relaxation times at the surface of the porous media. It thereby might be possible to exploited this effect for gaining information on the surface and surface near structures of porous media.

Concluding established methods can be can be feasible at high fields if certain obstacles are considered. Additionally diffusion relaxation seems a promising tool and has to be studied further.

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P25 **NMR Diffusometry and MAS NMR Spectroscopy of Functionalized Mesoporous Proton Conductors**

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Ordered mesoporous silicas are promising materials for creating hybrid organic-inorganic composites by functionalization with organic moieties showing high potential for application e.g. in optical gas sensing, catalysis, separation or fuel cells. The latter is in the focus for MCM-41 modifyed with different functional groups, for which high proton conductivities could be obtained which strongly depend on the type of anchorage, the degree and type of functionalization and the spacer chain length between the silica host and the imidazole group. In addition to previous structural characterization by powder X-ray diffraction, nitrogen adsorption, and FT-infrared spectroscopy, the present contribution show the investigation of the materials by magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy (^1H, ^{13}C, ^{27}Al and ^{29}Si) and MAS PFG NMR diffusometry. NMR self-diffusion coefficients were converted into conductivities by means of the Nernst-Einstein equation. Values obtained by this indirect approach were compared to the proton conductivities directly obtained by impedance spectroscopy (IS) on pressed powders, in order to establish a model for the proton transport in these materials.

P26 **Calcium Silicate Hydrate Gel Evolution of Mineral Endodontic Cements Studied by TD-NMR**

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The clinical use of mineral endodontic cements has increased in the past decade. The kinetics of the formation of the pore structure of the cements affects their clinical performance. In this study Time-Domain Nuclear Magnetic Resonance (TD-NMR) of ^1H nuclei is applied to compare the evolutions of T_1 and T_2 relaxation time distributions of novel endodontic cement pastes, followed from 1 hour after the preparation up to 30 days.

Measurements were performed approximately logarithmically distributed during the ageing time. Specimens were prepared by adding 250 mg of de-ionized/double-distilled water to 500 mg of cement powders. Three samples of two different White-Portland-Cement-based (WPC) endodontic cements were used:
1) TECH BIOSEALER standard (ISASAN s.r.l., Como, Italy), WPC with added calcium chloride which tends to cause expansion and increases the rate of setting and 2) TECH BIOSEALER fluoridated, WPC with added NaF and $CaSO_4$. Sodium fluoride gives F^- ions to the structure of the enamel of the tooth, and moreover it is known by practice that it makes the paste better workable for a longer time, while calcium sulfate controls the setting and slows

down the hydration. Bismuth oxide is also added to increase radio-opacity and phyllosilicates, as filler, to place water molecules at the disposal of the reactions. Data were acquired at 20 MHz and 25 °C. An inversion recovery sequence, with 128 t-values logarithmically distributed between 50 µs and 1.4 s, and a CPMG sequence, with 8000 echoes and 40 µs of echo time, were used. »Solid« signal, coming from low mobility protons, and »Liquid« signal, due to ^{1}H with higher molecular mobility, were separated on the FIDs and evaluated by means of a particular home-made algorithm. The determination of the »Solid« and »Liquid« signal amplitude permitted us to evaluate their ratio, an indicator of the hardening process of cement pastes. Quasi-continuous relaxation time distribution analysis of ^{1}H signals was performed by the in-house inversion software (UpenWin).

Strong and rapid changes of the TD-NMR parameters during cement setting were detectable for both cements. The »Solid« component increased at the cost of the Liquid one and T_1 and T_2 distributions of the »Liquid« component shifted towards shorter times with different kinetics for the two cements. The observed behaviors are consistent with the formation, in this 30-day period of hydration, of the solid matrix and of the buildup and evolution of the pore structure of the C-S-H gel. A different kinetics of the onset of the solid signal and a different final nanopore structure were observed for the two cements. The results showed that Time-domain NMR is a useful technique to observe and quantify the kinetics of solid matrix production and nanostructure formation and can be used to compare new endodontic cement pastes in order to optimize their performances.

$\boxed{\text{P27}}$ Calibrating d-PFG Filtered MRI Using a Novel Anisotropic Diffusion Phantom

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Introduction: Diffusion MRI methods can provide valuable microstructural information about tissues and porous media within an imaging volume [1-3], however, calibrating them is problematic owing to the lack of suitable anisotropic diffusion MRI phantoms. Here we constructed an anisotropic diffusion MRI phantom to calibrate diffusion MRI sequences and validate models that relate the diffusion MRI signal to the MRI pulse sequences and material microstructure. We then use this phantom to calibrate a d-PFG filtered MRI experiment to measure and map mean pore size [4].

Materials and Methods: This new phantom consists of four 2 mm thick water-filled glass capillary arrays (GCA) (Photonis USA). The nominal pore diameter of two wafers is 10 µm; that of the other two is 25 mm. D-PFG filtered NMR sequences were acquired by applying two wave vectors sequentially, and by varying the angle between them from 0° to 360°. A 7 T vertical-bore Bruker DRX

microimager was used with PFG NMR parameters: $d = 3.15\,\text{ms}$, $D = 75\,\text{ms}$, and G between 0 and $221\,\text{mT/m}$; and MRI parameters: $\text{TR/TE} = 7000/12\,\text{ms}$, $\text{FOV} = 30\,\text{mm}$ and slice thickness $= 2\,\text{mm}$. An operator-based modeling framework [5-7], which predicts the MRI signal attenuation due to restricted diffusion within packs of impermeable cylinders as well as a free water compartment for each d-PFG filtered MRI sequence, was used to estimate the pore diameter map. ROI analysis was used to measure the average pore diameter and pixel-by-pixel analysis was applied to create a mean pore diameter map.

Results and Discussion: ROI analysis of the d-PFG filtered MRI data yields a pore diameter of 27.7 ± 0.1 and $27.75 \pm 0.04\,\mu\text{m}$ for the 25 microns ID wafers and 9.94 ± 0.09 and $10.0 \pm 0.1\,\mu\text{m}$ for the 10 microns ID wafers. A composite GCA phantom, constructed by stacking wafers to produce a known distribution of pore diameters, can be used to calibrate diffusion MRI methods like AxCaliber [2].

Conclusion: While a variety of media have been used successfully to calibrate diffusion NMR experiments, this anisotropic phantom and its associated mathematical framework appears to be the first one to be able to calibrate diffusion MRI experiments, including single, double, and multiple PFG MRI or wave-vector based methods. Since the GCAs are stable over a large range of temperatures and are available in various pore sizes and wafer thicknesses and diameters, various embodiments of this phantom can be used in a variety of applications ranging from material sciences to clinical and biological MRI.

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P28 Physical State of Model Drugs in Mesoporous Confinement

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We investigated structural and dynamical properties of confined phases prepared by impregnating mesoporous SBA-15 and MCM-41 with solutions of indomethacin with various concentrations and in various solvents. Indomethacin, an anti-inflammatory drug, was chosen as a model compound, because it exists in a number of polymorphic and solvate modifications. In our study the physical state of mesoscopically confined indomethacin crucially depended on the concentration of the loading solution and varied from a molecular dispersion at low concentrations to a "crystalline" solvate state at high loading concentrations. The "crystallinity" was implied by well defined thermal transitions, very

similar to those of the bulk crystalline phases, and not by long-range order. The confined "crystalline" phases were formed only from solvate-forming solvents, because only supreme solubility of indomethacin in these solvents lead to sufficiently high local supersaturations needed for crystal nucleation in confined space.

As opposed to thermal transitions, NMR spectra of the confined phases exhibited features of glassy phases. These features could be a consequence of a high fraction of molecules at the surface of the crystallites. Atomic nuclei in the surface molecules namely resonate at shifted frequencies because they experience different local environments, and also relax differently because of different coupling with their neighbors and the lattice. Thus, although at first sight thermal analysis and NMR spectroscopy pointed to different physical states of the confined indomethacin, results of both techniques were not in a contradiction.

P29 Frequency Dependent NMR Relaxation of Polymeric Nanocapsules

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Understanding the surface effects on the dynamics of molecules confined inside polymeric nanocapsules is important both for obtaining of theoretical scientific knowledge and for designing of new nanocapsules to be used in controlled drug delivery [1]. Surface interactions give rise to orientational order near the surface with the molecules diffusing from the isotropic bulk region to the ordered surface layer and vice versa. At each return the molecules orientation is controlled by the interaction with the surface. Consequently, the dipolar correlation function is characterized by a slowly decaying part owing to the repeated returns of molecules to the surface. This mechanism of relaxation that is based on »reorientations mediated by translational displacements« (RMTD) [2] is the subject of our investigations.

The nanocapsules were produced using an interface polymerization technique [3]. This method involves the initial preparation of two phases: an organic phase and an aqueous phase. The organic phase consisted of a mixture of organic solvent (acetone), oil (Miglyol) and monomer (ethyl 2-cyanoacrylate). The aqueous phase contained a mixture of surfactant (Pluronic F 68) and distilled water. The mixture of organic phases was slowly injected through a needle into a magnetically stirred aqueous phase. This mixture immediately became milky and nanocapsules with different diameters were formed. Three types of nanocapsules with different concentrations of miglyol ($2\,\%$, $4\,\%$ and $6\,\%$) were produced and analysed in our work.

The relaxometric investigations were done at room temperature using a fast field cycling (FFC) Stelar instrument [2] and a high magnetic field Bruker instrument. The evolution of the longitudinal relaxation rate as a function of frequency between 0.01 and 300 MHz has indicated a strong influence of the miglyol concentration. The observed frequency dependence is assigned to the reduction in the mobility of the confined molecules by decreasing the miglyol concentration. The experimetal data have been compared with the theoretical values obtained on the basis of a RMTD theoretical model which allows the extraction of the characteristic correlation times.

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P30 Pulsed NMR Study of Carbon Adsorbents with Homogeneous Porosity Synthesized with Aluminum Oxide as a Template

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Carbon mesoporous adsorbents with a narrow pore size distribution are of considerable interest in view of their application both as electrodes for fuel elements and adsorption of large molecules (fibers, dyes and polymers). At present a template method of synthesis of such adsorbents is actively developed. Aluminum oxide matrix was used as a template for synthesis of carbon adsorbents of homogeneous porosity. Both a method and equipment were developed for a synthesis of a new transit form of aluminum oxide - a monolithic aerogel composed of 5 nm nanofibres of amorphous aluminum oxide. The density of porous monolithic alumina oxide (PMAO) is $0.4 \, \text{g/cm}^3$, the value of specific surface, S_{BET}, exceeds $300\text{–}400 \, \text{m}^2/\text{g}$. For the synthesis of homogeneous porous carbon adsorbents, aluminum oxide nanofibers were covered by a layer of polymer carbon precursors as petroleum pitch (PP), a resulted carbon composite PMAO-PP have been pyrolyzed. Afterwards, alumina matrix was removed by dissolution. Both water vapor and low temperature nitrogen adsorption measurements revealed that PMAO-PP adsorbent had a turbostratic homogeneous mesoporous structure with a pore size of 3.75 nm, S_{BET} was equal to $110 \, \text{m}^2/\text{g}$. Porous structure of PMAO-PP adsorbent was studied by pulsed NMR techniques. Free induction decay (FID) observed in initial PMAO-PP adsorbent after evacuation was approximated by a sum of three components corresponding to contributions from residual water molecules in pores and to protons included into PMAO-PP structure. Then PMAO-PP samples were saturated by cyclohexane that was

used as a probe in nmr cryoporometry experiments. A melting curve of cyclohexane in PMAO-PP pores was presented as a variation of intensity of slow decaying FID component with warming from 153 up to 238 K. A narrow pore size distribution in a range of 3–6 nm was defined in PMAO-PP. Cyclohexane diffusion in PMAO-PP pores was studied by means PMFG NMR method with a maximum PMFG value of 30 T/m. Several phases of cyclohexane with different mobility in pores of adsorbent were found. As the diffusion times increased a relative fraction of cyclohexane molecules in a phase with minimal self-diffusion coefficient ("slow" phase) reduced, but the initial slope of spin-echo attenuation was invariable, specifying the exchange processes between the "phases". The life time of cyclohexane molecules in the "slow" phase as well as a dimension of the phase were defined. The results of performed nmr experiments agreed with the data obtained by spectral and adsorption methods.

P31 NMR Reveals the Local Structure and the Chemical Properties of the Inner Surfaces of Mesoporous Materials

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Whether X-ray diffraction or NMR is more suitable to elucidate the structure of crystalline materials is a matter of debate. For amorphous materials, however, NMR is without competition. In this presentation we review our recent efforts to develop an NMR based experimental strategy to characterize the local structure and chemical properties of the inner surfaces of ordered mesoporous materials [1-3]. This strategy is relies on the study of chemically active surface sites, i.e., surface groups able to form hydrogen bonds either between each other or with guests. The chemical nature of these sites defines the properties of the inner surfaces. On the other hand, the chemical properties of these sites are affected by the local surface structure and the presence of adsorbed guests. Thus, the potential chemical reactivity of the inner surfaces, their local structure, and the distribution of guest molecules on the surfaces can be evaluated experimentally. In addition, these data can be used to model the structure of the materials under study.

The following topics will be discussed:

(i) Surface silanol groups, their number and distribution at the inner surfaces of pure siliceous MCM-41 and SBA-15 materials, their proton-donating ability and their accessibility for guest molecules [1,2];

(ii) surface functionalization of SBA-15 materials with different functional moieties, and a checklist of generic properties for atomic-scale models of periodic mesoporous silicas [2];

(iii) ordering of adsorbed water molecules at the inner surfaces of sulfonic and phosphonic acid functionalized SBA-15 silica, and the effect of this ordering on

the proton-donating ability of the functional moieties [3].

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P32 Permeability of Modified Polyelectrolyte Capsules Studied by PFG NMR

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Polyelectrolyte microcapsules can be prepared from strong polyelectrolytes on silica particles by using the layer-by-layer (LBL) self assembly method [1]. Subsequently, the silica core is dissolved with dilute hydrofluoric acid. The obtained microcapsules are a promising material that can be used for example as drug delivery systems in medical application [2,3]. For this aim detailed knowledge about the capsule wall permeability is needed that can be obtained by pulsed field gradient (PFG) NMR. With this method the exchange behaviour of a probe molecule through the capsule wall can be analysed. With performing diffusion experiments at different diffusion times D biexponential echo decays are observed that depend on D. With applying a global fit over all echo decays an exchange time tex can be obtained that characterizes the capsule wall permeability [4].

The aim of this work is to modify the wall of $(PAH/PSS)_5$ capsules by adsorbing layers of different polymers on the capsules in order to change the permeability of the capsule wall. For the additional coating the polymers PM2VP-b-PNiPAm, P2VP-b-PEO and a lipid bilayer of DPPC/DPPA are used. We obtain modified capsules that differ in the adsorbing material and in the number of the additional layers. Another modification is to heat $(PAH/PSS)_5$ capsules to 80 °C for one hour, cool down the sample to room temperature and then perform the measurement. For all diffusion experiments on the modified capsules PEG ($M_W = 1000$ g/mol) is used as a probe molecule.

From the diffusion experiments the exchange time for PEG in dispersion of differently modified capsules is calculated. An obvious trend is found: PEG

in unmodified capsules has a significantly lower exchange time than PEG in presence of modified capsules. The largest exchange time and therefore the smallest wall permeability is shown for the lipid coated capsules. There even water shows slow exchange. Only a small effect on the wall permeability is shown for the heat treated capsules.

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P33 NMR Studies of the Mobility of Carbon Dioxide and Hydrocarbons in Nanoporous Coordination Polymers

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Metal-organic frameworks (MOF), which belong to the class of coordination polymers, are crystalline three dimensional networks of relatively small organic linker molecules connected via metal cations acting as coordination centers [1]. In the present study, we introduce NMR studies of diffusion and relaxation of molecules adsorbed in three different types of such crystalline nanoporous coordination polymers.

In the MOF CuBTC (1300 m^2/g, diameter of largest pore $d_\mathrm{p} = 0.9\,\mathrm{nm}$) the metal coordination centers consist of non-paramagnetic Cu_2 dimers. Relaxation time studies of adsorbed alkanes and carbon dioxide show that the transverse and the longitudinal relaxation times are rather short compared to other microporous systems with similar pore size. Obviously, there is a strong paramagnetic contribution to the total relaxation in these host-guest systems. Structural defects in the CuBTC framework in which a part of the Cu^{2+} ions are not present as dimers are the origin of these paramagnetic interactions. Self-diffusion coefficients measured by PFG NMR are found to be in the range of $10 \times 10^{-11}\,\mathrm{m}^2/\mathrm{s}$ to $10 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$ with activation energies consistent with those predicted in MD simulations [2].

In the IRMOF-1 (2900 m^2/g, $d_\mathrm{p} = 1.2\,\mathrm{nm}$, Zn^{2+} coordination centers, also referred to as MOF-5) diffusion studies with adsorbed benzene were performed by the 13-interval sequence and diffusion relaxation correlation measurements. At low concentrations, the experimentally determined self-diffusion coefficients in the intact IRMOF-1 pore system agree very well with data obtained in MD simulations [3,4]. However, at higher benzene concentrations, the NMR data evidence clustering of benzene molecules in this large pore MOF systems, which has not yet been included in the MD simulation models for this host-guest system [4].

The very new IMOF-1 ($800\,\mathrm{m}^2/\mathrm{g}$, $d_\mathrm{p} = 0.38\,\mathrm{nm}$, Zn^{2+} coordination centers [5]) forms a pore system of one dimensional channels. PFG NMR spin echo attenuations with adsorbed methane (^{1}H NMR) and carbon dioxide (^{13}C NMR) are consistent with anisotropic diffusion of the guest molecules in the pore system. However, single-file diffusion which might be expected for methane with a kinetic diameter closely fitting the pore diameter, could not be evidenced in the time dependent measurements. Thus, the pore structure or the effective pore diameter of the IMOF-1 needs to be refined in such a way that it allows passing of the methane molecules in the individual pores.

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P34 Characterization of Polyol-Stabilized CaF$_2$ Nanoparticles and Structural Investigations by Nuclear Magnetic Resonance Spectroscopy

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Conditioning and functionalizing the surface of nanomaterials are key-issues to control properties as shape, size, catalytic activity, luminescence, electrical conductivity, biological reception and uptake. Here, polyol-stabilized nanoscale calciumfluorid particles were obtained and characterized with state-of-the-art analytical methods as dynamic light scattering (DLS), electron microscopy (SEM, TEM), high-resolution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD), Fourier-transformed infrared spectroscopy (FT-IR), sorption analysis (BET), thermogravimetry (TG) and electron spin resonance (ESR). Particle size/shape, size distribution, materials composition and crystallinity were investigated. The first time these calciumfluorid nanoparticles were characterized by multinuclear multidimensional liquid and solid nuclear magnetic resonance (NMR) spectroscopy. New core-shell - surface, interface and interphase interactions were elucidated. A mobile phase of diethylene glycol (DEG) bond to a mobile surface component of CaF$_2$ on top of the crystalline core of the nanoscale particles were observed. With the NMR data it was possible to estimate the thickness of the DEG/CaF$_2$ layer and to identify the surface binding. Paramagnetic lattice defects were recognized and applied for structure determination applying pseudo contact shift.

5.3 Fluids in Porous Media (Including Supercritical and Complex Fluids)

P35 **Chemical Composition Measurements in Trickle Bed Reactors Using ^{13}C-DEPT NMR and Partial Least Squares Regression**
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Trickle bed reactors (TBR) are important in industrial gas-liquid-solid reactions. TBRs columns are packed with catalyst particles, forming a porous structure with two length scales: the intra-particle pores within the catalyst and the inter-particle voids. Gas and liquid are supplied to the top of the TBR, flowing co-currently downwards within the inter-particle pores, and accessing the intra-particle pores by diffusion. Quantification of chemical composition in both inter- and intra-particle pores is essential to understanding conversion and selectivity in TBRs.

In this work, we show how ^{13}C Distortionless Enhancement Polarisation Transfer (DEPT) spectroscopy and Partial Least Squares Regression (PLSR) were used to measure the inter- and intra-particle compositions using natural abundance of ^{13}C reactants. Direct analysis of the ^{13}C DEPT spectra does not yield quantitative compositions due to local susceptibility variations and to the short relaxation times of the species present within these reactors. The PLSR approach works by forming quantitative relationships between ^{13}C spectral data and mixtures of known chemical concentrations; these relationships are then applied to real catalytic reaction data obtained from a TBR, enabling the chemical composition in the inter- and intra-particle space of the catalyst pellets to be determined.

Data will be presented for the hydrogenation-isomerisation of n-octene in a TBR. Experiments were carried out in a 4.7 T Bruker DMX200 spectrometer equipped with a 63 mm ^{1}H-^{13}C dual resonance coil. The TBR was packed with 1 % Pd/Al$_2$O$_3$ catalyst trilobes. ^{13}C-DEPT spectra were acquired in calibration experiments performed on flowing liquid mixtures of known concentrations of reactants and products. The spectra acquired for both inter- and intra-particle species were used to build the PLSR models. The PLSR was shown to measure both inter- and intra-particle chemical compositions with accuracies better than 5 % mol.

Gas chromatography was used to measure the conversion of n-octene in the TBR exit stream as a function of the inlet temperature and pressure of the reactants. For each set of operating conditions, and hence conversion, the difference in mole fraction of n-octene between the inter- and intra-particle spaces was determined. As conversion increased, the difference between inter- and intra-particle mole fractions increased from 1.5 % mol (for 2.6 % conversion) to 18.4 % mol (for 6.1 % conversion). These data provide a direct experimental

measurement of mass transfer limitations in reaction engineering, which control the formation of concentration gradients between the inter- and intra-particle pores and limit the observed reaction rate. Mass transfer rates are affected by the characteristics of the inter- and intra-particle porous structures. These new measurements will enable the quantification of mass transfer effects and hence aid the design and manufacture of more efficient catalytic materials and reactors.

P36 3D MRI of Cavitation in Pipe Flow

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A liquid flowing in a pipe will experience pressure variations due to changes in the pipe geometry. For a sufficiently fast flowing liquid, the local pressure can drop below the vapour pressure of the liquid, which results in the formation of bubbles (cavitation). This is a concern for chemical and biological applications as the collapse of these bubbles can erode the pipe wall. The measurement of this phenomenon requires a non-invasive and non-optical technique; therefore, it is well suited for study via magnetic resonance imaging. We used a motion-sensitised version of the SPRITE sequence, as it is capable of measuring fast flows and turbulent systems with no artifacts due to B_0 inhomogeneity or susceptibility variations. In this study, three-dimensional density maps were acquired at varying flow rates that allowed us to measure how the void fraction changed with flow speed. Three-dimensional velocity maps were also acquired.

P37 Relaxation of Polar and Nonpolar Molecules Confined Inside Partially Saturated Porous Media with Ferromagnetic Impurities

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Owing to its completely non-invasive character, nuclear magnetic resonance (NMR) is widely used to investigate the dynamics of molecules confined in porous media. NMR measurements of relaxation times and diffusion coefficients render quantitative data on the dynamics of confined molecules and the restrictions the confinement imposes on their translational and rotational mobility [1]. The interpretation of the experimental results of a diffusion experiment and their comparison with the theory or simulation rely on the assumption of a specific distribution of molecules inside pores and the consideration of internal gradient effects [2]. That is why, in the present work both the liquid morphology inside porous media with micrometer pores partially saturated with polar (water, acetone, ethanol) and nonpolar (cyclohexane, hexane, tetradecane) molecules and the role played by the internal fields in relaxation measurements was considered. To elucidate the role played by the internal gradients in a diffusion or relaxation experiment porous ceramics (1–10 µm pores) produced in our laboratory with

different volume densities of ferromagnetic impurities were examined. The results were compared with those obtained on commercially available Vitrapor-5 porous glass (1 μm pores). All relaxation experiments were performed in low fields using a Bruker MINISPEC spectrometer, operating at a proton resonance frequency of 20 MHz. The relaxation time distributions were extracted using a regularized numerical Laplace inversion algorithm (CONTIN) [3]. The experimental results were compared with a two phase exchange model providing us information on liquid morphology under partially saturated conditions and the influence of the internal fields on experimental results.

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P38 Nuclear Magnetic Resonance Logging While Drilling: From an Experiment to a Day-to-Day Service for the Oil Industry

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In oil and gas well logging Nuclear Magnetic Resonance (NMR) has long been considered to be an extraordinary measurement method because of its complex physics, difficult job preparation and the highly trained people required for data processing and interpretation. It was only used when other measurements failed to give the complete answer. With recent developments in the field of NMR Logging While Drilling (LWD), more standard applications became feasible.

The development of slim-hole NMR LWD technology expanded the range of applicable hole sizes from $9^1/_2$ in. down to $5^3/_4$ in. diameter holes. Today, with the invention of NMR data compression and improved telemetry rates, real-time data while drilling can be of similar quality to memory or wireline (logging after drilling) data.

One can see differences in the area of NMR applications between wireline and LWD. Wireline technology was developed toward high-end applications comprising all options offered by NMR physics. These applications include diffusion characterization and two-dimensional evaluations, as well as multiple frequency and multiple wait-time measurements. In contrast to this tendency, the LWD technology was developed toward everyday applications, vastly simplifying the complicated measurement concepts developed by wireline counterparts.

LWD tools need to be designed to be motion-insensitive, which was achieved by using low magnetic field gradients of approximately 2 G/cm and short inter-echo time in the CPMG-like NMR echo sequence. This yields straightforward

preparation and execution of the job as well as an easier interpretation of the measured data. For instance, gas and light hydrocarbon detection became feasible by direct observation of the T_2 distribution. Sophisticated approaches using T_1 or diffusion measurements are not required. Thus, we only consider designs acquiring T_2 data with low field gradients to be appropriate for everyday LWD applications.

In our poster we show the evolution of NMR LWD technology from a niche product to a day-to-day service. We illustrate this process through recent case histories.

P39 Multi-Scale Moisture Transport in Hardened Cement Pastes and Reference Porous Silicate Materials

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Improving sustainability and performance of cements is a key point to limit CO_2 emission. Long term durability is closely related to unsaturated moisture transport at different length scales of these materials.

In our study, hardened cement pastes exhibit threefold hierarchy: intra-CSH (hydraulic binder) nanopore, mesopore structure at a scale ranging from 3 nm to 20 nm and capillary pore network above 100 nm. The moisture transport at different water filling controlled by temperature and relative humidity ratio is followed by a proton NMR multi-scale approach using PFG diffusometry, field cycled relaxometry and spectroscopy correlated with T_1, T_2 and T_{1r} measurements. In parallel, a similar study is conducted in three types of reference pore network, having nano, meso and macro pore network MCM41, VYCOR, and controlled pore glass CPG respectively. The role and the efficiency of the three scales on the moisture transport are reported.

P40 Molecular Transport on Surfaces - Access to Surface Heterogeneity

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Providing high transport rates and high surface area, nanoporous materials are presently becoming an important ingredient of chemical industry. The efficiency of these materials is further determined by flexible tunability of their structural and surface functionalities, offering promising options for the process-oriented optimization of their properties. During the last years, a great variety of novel mesoporous materials with quite different morphologies of the pore networks and chemical compositions of the solid framework have been synthe-

sized. This, in turn, requires further development of proper techniques for their complete characterization. This concerns both transport properties of adsorbed species and, importantly, their specific surface interactions with intrapore surfaces. Pulsed field gradient (PFG) NMR [1] is a unique experimental tool, which may provide comprehensive information on molecular behaviour in porous matrices [2]. Recently, we have demonstrated that due to their sufficiently high surface area, mesoporous adsorbents can accommodate molecular ensembles accessible by NMR, including the range of sub-monomolecular coverages [3]. In particular, for the first time, we demonstrate that in this way, one may probe surface diffusivities down to 5 % of the monolayer coverages. As the most interesting result, we obtained that patterns of surface diffusion of organic molecules at different surface coverages in mesoporous adsorbents are drastically different from those on homogeneous metal surfaces. The observed behaviour is quantified as a direct consequence of surface heterogeneity and is discussed within the theoretical framework of the site-energy disorder [4].

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P41 Low-Field High-Pressure NMR Porosimetry

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In many applications of porous materials, the pore fluids (liquids or gases) are confined to the respective porous host system at elevated temperatures and pressures. For example, adsorption, storage and transport of methane, hydrogen, carbon dioxide and other gases at high pressures is of particular interest in many fields of chemical, environmental and reservoir engineering. In this contribution we introduce the experimental set-up for low-field NMR relaxation and NMR diffusion studies of porous materials at static pressures of up to 30 MPa and we demonstrate its successful applications in in-situ characterization of pore space properties of nanoporous adsorbents such as carbon black and metal-organic (MOF) frame works as well as for reservoir rocks.

In our high-pressure NMR porosimetry approach, the respective samples are exposed to the elevated gas pressures by a home-build apparatus constructed of stainless steel HiP Taper Seal parts and of a non-metallic, NMR compatible pressure-resistant sample vessel made of the high-tensile plastic PEEK. The sensitive sample volume inside the pressure-resistant vessel is a cylinder of about 10 ccm. The low-field NMR spectrometer for the relaxation time studies consists of a MARAN DRX console equipped with a home-build shimmed NdFeB permanent magnet arrangement generating a magnetic flux density of 0.119 T (^{1}H resonance frequency of 5 MHz) [1].

In the experiments with carbon black and MOF CuBTC [2], the T_2 relaxation time distributions show well distinct peaks for the high pressure methane gas phase surrounding the nanoporous particles and those adsorbed in the pore space. These NMR signals change characteristically in intensity and T_2 when changing the methane pressure. Co-adsorption of carbon dioxide leads to replacement of methane by the stronger adsorbed CO_2, which could be followed by ^{1}H NMR. These observations allow the measurement of adsorption isotherms at elevated pressures and the assignment of preferred adsorption sites in the porous host material.

In the porous reservoir rocks, shifts of the T_2 distribition of the pore water were observed, when the water-saturated rock sample is exposed to high CO_2 pressures. These shifts are caused by dissolution of minerals due to changes in the acidity when CO_2 is dissolved in the pore water [3]. Methane adsorption at high pressures in low-porosity sedimentary rocks allow us to distinguish between the gas phases and adsorbed phase and may be used to quantify the methane storage capacity of such materials.

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P42 Water Migration in Multi-Layered Coatings

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Coatings are applied for esthetical and protective reasons on cars, planes, walls, furniture, etc. Coating formulations and their end properties vary from application to application. Many coatings consist of several layers, each giving a specific functionality to the coating. In the past two decades water-based products have emerged on the market. There is a demand for knowledge of these water-based products: structure formation and water ingress.

Progress has been hampered by a lack of experimental techniques for monitoring processes inside a coating. The techniques used in coating science only give access to averaged or surface properties. In case of multi-layered coatings information on the water distribution is crucial. Since the thickness of an organic coating is of the order of 10–100 µm, conventional MRI techniques cannot be used. However, the GARfield method [1], enables the study of coatings with a resolution of 3–5 µm.

The present study addresses the water uptake by multi-layered coatings [2]. Two-layer coatings, consisting of a waterborne basecoat and a solventborne top

coat, were used as model systems. The basecoat consisted of fused polymeric particles. The swelling of and water distribution in these coatings were measured with a GARField set-up [3]. Water profiles were calibrated with gravimetry. With T_2 spectra the state of water during uptake and its plasticizing effect on the polymer matrix were analysed.

Water accumulated in the basecoat layer and that the top coat acted as a barrier. Drying rates were much faster then uptake rates. A model was developed based on the osmotic pressure in the basecoat layer and the diffusivity in the top coat. The barrier properties of the top coat were obtained from D_2O/H_2O exchange experiments. Osmotic pressure curves were obtained from sorption experiments with PEG solutions having different water activities. With these experiments we were able to predict accurately the drying properties of the system. The assymetry between sorption and drying rates could be explained with the non-linear properties of sorption isotherms.

With T_2 relaxation spectra we could distinghuish the signal coming from water and polymer. The diffusivity of water in the base coat was determined from these spectra. It reached values close to $10^{-10}\,\mathrm{m^2/s}$, indicating that the water was highly mobile and located in between the polymeric particles. In the spectra a long relaxation time appeared during water uptake, which seemed to ^{1}H connected with polymeric chains. Tiny amounts of water, entering the polymeric particles, plasticized these particles leading to an increase in the polymer mobility.

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P43 **Using NMR Propagator Measurements to Probe CO_2 Entrapment in Porous Media**

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The geological sequestration of CO_2 in rock formations such as saline aquifers is seen as a potential climate change mitigation technique. One physical mechanism by which this could occur would be the capillary or residual trapping of discrete pore-scale CO_2 bubbles (often referred to as ganglia) in the pore space.

In this work, nuclear magnetic resonance (NMR) techniques were used to quantify the spatial distribution and pore environment of such CO_2 entrapment arising from the flow of a carbonated brine ($2\,\mathrm{wt\,\%}$ KCl) solution in a model porous medium (random $100\,\mu\mathrm{m}$ glass bead packing). 2D spin-density images of water in the sample cross-section revealed a relatively macroscopically homogeneous CO_2 entrapment, whilst being unable to spatially resolve the CO_2 ganglia pore environment. This was achieved using NMR displacement propagators (probability distributions of displacement) of water, acquired us-

ing pulsed field gradient techniques before and following CO_2 entrapment. The propagators showed an increase in mean displacement after CO_2 entrapment corresponding with a reduction in water-occupied porosity of 15 %, an observation which was quantitatively supported by 1D NMR spin-echo profiles of water in the superficial flow direction.

A numerical propagator simulation strategy based on the Lattice Boltzmann (LB) method and random walks was used to facilitate interpretation of the propagator statistics and shapes, as acquired before and after CO_2 entrapment, by considering various pore environments in which CO_2 could become trapped. Comparison with the corresponding experimental data suggests that CO_2 is preferentially entrapped in large pores.

P44 Fluid Dynamics on Undisturbed Soil Sample Investigated by NMR

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We used magnetic resonance (MR) imaging and MR relaxometry measurement techniques to study the process of infiltration and nickel transport in an undisturbed soil sample of coarse sandy loam taken into the plexiglas cylinder. The changes in entrapped air distribution and its impact on steady state flow rates were studied by repeated ponded infiltration experiment. The main stages of each experiment run (wetting, steady state flow, drainage) were monitored by multi-echo multi-slice MR sequence. T_1/T_2 mapping was performed during steady state conditions (steady state flow, steady state after drainage). Later the nickel nitrate pulse was injected with the aim to visualize the solute breakthrough. Moreover, the soil sample was scanned with computed tomography, the CT images were obtained before and after magnetic resonance (MR) investigation. Then potential preferential flow paths identified in CT were compared with actual flow path visualized in MR scanning.

The novelty of this approach is the 3D visualization of infiltration process and nickel transport in natural soil sample, along with simultaneously acquired tensiometer readings and breakthrough curves. It reveals its potential to study the complex flow dynamics. Differences in flow process in both infiltration runs are significant and the results of MRI, flow and transport observations are consistent.

P45 Rapid Imaging of the Hydration of Surfactant Formulations

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The motivation to investigate the hydration of fabric detergent powders is

driven predominantly by environmental factors. With increasing levels of water consumption worldwide there is a desire to use less in the wash cycle. Water used in laundry washing also requires heating, and hence a large additional energy input. There is therefore a desire to perform washing at lower temperatures. Detergent manufacturers face the challenge of producing detergents which provide suitable cleaning performance at lower temperatures and with a lower water load. Added to this is the habit of many consumers to use less powder than the stated dose (due to powder residue being left on clothes or in the detergent drawer). Hence, it is desirable to model the hydration behaviour of detergent powders at a fundamental level across a range of lengthscales.

We seek to use NMR techniques to describe and model the hydration of the detergent powder primarily at various lengthscales. Work is performed at the bulk scale to investigate macro-scale factors involved in the hydration by tracking ingressing water. RARE [1] imaging has been used to monitor qualitatively the ingress of water into a bed of detergent at flows up to 10 ml/min. The formation of a hydration induced barrier to further ingress has been indirectly observed. This confirms the hypothesis that water can react with the surfactant to form a gel which hinders the further dissolution of detergent. Data is gathered with the aim of developing a model of the hydration of detergent powder and constructing a model powder draw in-situ in the magnet. Characterisation of simplified detergent mixtures has been successfully performed, Rapid acquisition techniques for T_1 (2-shot T_1) and D (DIFFTRAIN) [2] have been validated for use in hydrating systems by way of a direct comparison with standard experiments. The work performed forms the basis on which quantitative structural determination of hydration can occur, using tools such as quantitative RARE imaging and spatially resolved T_1 and D measurements.

The primary challenges presented in the use of NMRI are associated with obtaining sufficient spatial and temporal resolution. Surfactant hydration occurs in the space of minutes and so robust rapid acquisition techniques must be used to quantitatively monitor water ingress. There is also the potential to use ^{23}Na NMR due to the use of Sodium Linear Alkylbenzene Sulphonate (NaLAS) as the main anionic surfactant used within the detergent. This would allow direct tracking of the surfactant present.

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P46 Induced Surface Modifications on Core Plugs Followed by NMR Relaxometry

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In order to increase the oil productivity or in case of early water production or well performance declining is necessary to operate some specific chemical processes in the formation. The use of chemicals in the well operations is very critical and cost effective. For this reason an intensive laboratory evaluation on specific rock cores and especially the effects of the chemical treatments on the surface modifications and wettability changes are widely applied in addressing the performance of the technical operations.

NMR relaxometry techniques were applied as a non destructive aid to clarify the mechanisms related to the rock-fluid interactions. As well known, the relaxation times are related to the interactions of the protons present in the oil and water molecules with the neighbouring environment inside the porous medium. Differences in the T_2 and T_1 values measured before and after the saturation step can give information regarding the different distribution of fluids and their interactions with the porous matrix [1]. Several saturation tests were performed using sandstone and limestone core plugs saturated with a real reservoir crude oil and brine, aged for several days and then subjected to chemical treatments by flooding with specific solutions containing different surfactants and polymers. Every experimental step was followed by NMR relaxometry to get information on fluid distribution alterations inside the rock matrix. The NMR analysis was complicated by the use of a very viscous oil and the results obtained are discussed.

However, NMR relaxation measurements showed significant differences for the different treatments (as shown in the T_2 plots reported). In particular, some polymer and surfactant formulations were found to appreciably recover the fluid distribution inside the porous matrix even after a very long aging process in crude oil. This evaluation was possible by the application of a wettability index algorithm [2]. A critical examination of the results and the possible technical developments are described and discussed in detail.

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P47 **Diffusion and Advection Effects on 3D Tracer Distributions in Heterogeneous Porous Media**

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Diffusion experiments, involving the migration of H_2O into D_2O-saturated porous samples, are performed. Three-dimensional data, from SPRITE MRI experiments on a heterogeneous sandstone, are interpreted with the aid of MIN3P-D - a multicomponent reactive transport code.

For a heterogeneous sample with a relatively high permeability, our simulations clearly demonstrate the pronounced effects of density-driven advection on H_2O migration. This technique, based on MRI measurements and simulations, is well capable of demonstrating and characterizing the 3D nature of diffusion and tracer migration on the scale of observation, with no influence from reaction processes.

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P48 **MRI Measurement of the Void Fraction and Velocity Field in an Acoustically Cavitated Liquid**

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Acoustic cavitation is the process of gaseous bubble formation, growth, and collapse due to a sudden pressure drop in the liquid caused by a strong acoustic field. Void fraction, the volume of the cavitated liquid occupied by formed bubbles, is an important parameter in acoustic cavitation. Here we introduce a Magnetic Resonance Imaging (MRI) based technique for void fraction measurement in the acoustically cavitated liquid.

The magnetic susceptibility effect in the liquid that surrounds the gaseous bubbles leads to T_2^* change in the liquid. Using the pure phase encoding 3D Conical SPRITE sequence, the MRI signal in the form of $M_{zo}\sin(\alpha)e^{(-t_p/T_2^*)}$ was collected for a $64 \times 64 \times 64$ image at 8 phase encoding times t_p from 0.1 to 2 ms. Then a two-coefficient exponential curve was fitted through the acquired datasets to find the T_2^* and spin density within each image pixel (with

the uncertainty lower than 1 %). Finally, the void fraction was measured by subtracting the spin density maps of the non-cavitated and cavitated forms of the same sample.

In addition, we measured a 3D velocity field of the system using Motion Sensitized Conical SPRITE and calculated the divergence and vorticity of the velocity field. Using the void fraction and velocity field information, we estimated the compressibility degree of the cavitated fluid and its effect on the flow. The two techniques were applied to two different samples with various bubble dynamics: water and water with addition of 1mM of a surfactant to investigate the surfactant effect on the cavitation process.

P49 Dynamics of Ionic Liquids in Porous Media Studied by NMR

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Molten salts with melting points in the proximity of the room temperature are commonly known as Ionic Liquids (ILs). In recent years this new class of substances has become available for, among other applications, reaction-controlling solvents, electrolytes for batteries and fuel cells, as well as green solvents for extraction processes in field as diverse as cellulose treatment and food processing [1]. Their physico-chemical properties like negligible volatility, nonflammability, chemical and thermal stability and high ionic conductivity, can be easily tuned due to the great number of combinations between anions and cations and/or simply by changing the structure of the components ions. Many of the different properties of this kind of solvents are due to their ionic character making them useful in the fuel cells applications. The study of their molecular motions in porous media is therefore relevant in order to understand the transport properties in this kind of materials. Reorientation and translational dynamics can be suitable studied by Nuclear Magnetic Resonance (NMR) Relaxometry and Diffusometry [2]. In this contribution a study of the dynamics of imidazolium derivatives ILs in bulk state and under confinement in mesoscopic porous materials is presented. T_1 relaxation was measured at different temperatures in the frequency range from 10 kHz to 30 MHz with a Stelar FFC relaxometer and complemented with a relaxation value at 300 MHz. Strikingly, the longitudinal NMR relaxation mechanism between the bulk and confined solvent is different at room temperature but becomes similar when the temperature is reduced below the melting point close to the glass transition temperature. The dynamics of the different ions can be studied in the case when the imidazolium derivatives anion contains ^{19}F. This makes possible to discuss interactions between different ions and the confining pore walls. The data are correlated with the translational dynamics obtained via diffusion measurements [3]. Diffusion measurements were carried out in the stray field of a single sided NMR device (MOUSE). They show differences in the diffusion constant of the anions and cations. This difference reveals an anomalous behaviour (reported as well in

literature [4]) in the sense that the ion with larger hydrodynamic radius appear to have the small diffusion constant.

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P50 Imaging Fluid Displacement in Porous Media Using T_2 Mapping SE-SPI

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Magnetic resonance imaging is an effective method for the characterization of fluids in the pore space of rock cores. The T_2 distribution of a rock core is directly related to the pore size distribution within the core. Long T_2 values represent large pores, while short T_2 values represent small pores when measuring the T_2 value of a wetting fluid. We employ T_2 mapping Spin Echo Single Point Imaging (SE-SPI) [1] to obtain spatially-resolved T_2 distributions of three reservoir core samples. A chalk, limestone and Bentheim core were saturated with an H_2O brine solution and subsequently flooded with a D_2O brine solution. T_2 mapping SE-SPI measurements were obtained for the duration of the flooding process. Fluid content in large, small and dead-end pores throughout the water flood was monitored by the changes in the T_2 distributions. Characteristic changes in the T_2 distribution were observed between the three cases. The three samples revealed flooding behaviors that were broadly similar but different in detail.

Graue, et. al. have performed similar displacement studies of brine solutions in rock cores [2,3]. Radiation intensity from nuclear tracers was monitored to measure water saturation across chalk and sandstone cores. The advantage of employing the T_2 mapping SE-SPI technique to core measurements is that in addition to spatially mapping the water saturation, changes in pore size occupancy are revealed.

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P51 **Diffusion of Ionic Fluids in Porous Media Studied by Unconventional Diffusion NMR Techniques**

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Beside the standard stimulated spin echo sequence several unconventional NMR techniques have been introduced to study self diffusion of liquids, all of them exhibiting characteristic limitations regarding the time scale and systems that can be studied. By combining several complementary techniques the accessible range of studied time scales can be expanded significantly. In addition to them, two-dimensional correlation experiments sensitive to relaxation times and diffusion coefficients help to study molecular transport in porous media in detail. Two NMR pulse sequences are used. The first one consists of a modulated gradient spin echo with CPMG sequence in a constant magnetic field gradient, which provides information about molecular diffusion in the frequency domain. The second one is a modified CPMG sequence that allows the determination of molecular displacements as a function of time. Both techniques are used to study molecular transport properties of complex fluids like ionic liquids confined in porous media with characteristic pore sizes ranging from several μm down to the nm range. A time dependent diffusion constant is observed. The influence of the geometrical confinement and the interaction between the ionic molecules and the pore walls in the transport properties can be studied.

P52 **NMR Relaxometry and Imaging of Polymer/Cement Dispersions**

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Cement-in-polymer dispersions (p/c) consist of a water or alkali soluble polymer and non-hydrated cement. These newly developed materials are used as coatings for various systems of rovings, leading to the formation of highly resistant composites designed for demanding applications in the building industry. The formation of the composite matrix is triggered by hydrating the p/c dispersion; the contact with an aqueous environment leads to the solvation of the polymer and, subsequently, to the exposure of the cement particles. No information is yet available on the properties of the composite, such as porosity, transport times or the behaviour of fluxes of matter, information known to be essential for predicting the materials behavior and resistance.

In the present study, relaxometry and imaging experiments performed on hydrated poly(vinylacetate)-poly(vinylalcohol)/cement dispersions with different compositions are used to obtain information about the composite microstructure. It is already common knowledge that hydrated cement-based porous materials present multiple relaxation modes. The most widely used model for data interpretation is the three phase model: bounded water, gel water and capillary

water [1], although more complicated models also exist. The relaxation times of the phases depend directly on the pore size distribution and can thus be used for obtaining information about the pore size. Relaxation time measurements were performed during the hydration and hardening of the samples in order to follow the evolution of the cement microstructure, using the Inverse Laplace Transform.

The results exhibit multiple relaxation modes, corresponding to the organic components and to water located in different classes of pores. The diffusion of water in the hardened samples has been monitored in real time using ^{1}H NMR spectroscopy and single point imaging. The diffusion phenomenon has been observed indirectly, by immersing the H_2O saturated samples into D_2O. The relaxation parameters of the water protons have allowed the acquisition of SPI profiles of the water in the composites with sufficient temporal resolution to monitor the decrease of the H_2O signal as the water molecules were being replaced by D_2O. The apparent diffusion coefficient (D_{app}), which is mainly dependent on the curing, pore sizes and the presence of micro cracks, was determined for the composite specimens using data acquired at several temperatures.

The results have been processed based on a 1D theoretical diffusion model [2] that allowed the determination of the D_{app} spatial distribution. The values obtained from the temperature measurements were used to estimate the apparent activation energy for the diffusion process.

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P53 The Behaviour of Gypsum and Concrete Under Fire Conditions as Studied by NMR: The First Direct Proof of Moisture Clogging

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One of the most extreme examples of moisture related damage to building materials is fire spalling. If a fire occurs in a tunnel or building the materials will be heated up to well above 100 °C within minutes, rising up to even 1200 °C. As a result the moisture will start to boil in the material. However due to its low permeability the vapor transport is hindered and a large pressure can built up in the material. This pressure can ultimately lead to the explosion of the material during fire. This phenomenon has been especially observed for concrete in the various tunnel fires during recent years.

In order to study the moisture transport in building materials during extreme heating a special Nuclear Magnetic Resonance setup was built. This setup can be placed inside the magnet of a 1.5 T MRI scanner. With this setup one dimensional moisture profiles can be measured non-destructively while heated up to well above 500 °C with heating rates of up to 10 °C/min. The setup

can handle representative samples up to 8 cm in diameter and 10 cm in length. The measured NMR signal is corrected on basis of Curie law and the observed temperature dependence of the relaxation mechanisms in the porous material. It was found that the NMR signal can also in the case of gypsum indicate the dehydration state. The measured moisture profiles during the fire simulations runs for gypsum and concrete show the build up of a moisture peak just behind the boiling front, i.e., a peak is built up due to vapor condensation. This has been to our knowledge the first direct off proof of this so-called moisture clogging

P54 NMR Imaging of Water Flow in Packed Beds

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Measurements by magnetic resonance imaging (MRI) of water flow in granular porous media are presented in this study. Our goal was to obtain accurate measurements of interstitial and averaged velocities in packed beds. The flow cell consisted of two concentric tubes, with the inner tube (16.5 mm inner diameter) containing the packed bed and the outer tube defining an annular space (20.15 mm–26.15 mm in diameter) for the fluid return. Packed beds of different size and nature was placed in the inner tube and fully saturated with water. A gravity flow of water between two constant-head reservoirs was established through the packed bed. The geometry of the flow cell was chosen to enable comparison by the MRI method between volume flow rates of water in the porous media and in the outer annulus.

All MRI experiments were performed using a Bruker Biospec 2.4 T magnet. Spin-echo imaging sequence with flow-encoding gradient are used to acquire the spatial distribution of flow velocity. In porous media the spin-echo sequences are known to give better results than gradient-echo sequences because of their lower sensitivity to solid-liquid interfaces and magnetic susceptibility effects. The calibration of the MRI velocity measurements was achieved from Poiseuille flow in a tube at different flow rates. It was found that the MRI measurements reproduced the velocity profiles of Poiseuille flow with an accuracy better than 3 %.

To test the reliability of velocity measurements in porous media two situations were considered. In the first case, measurements were made on packed beds with large diameter beads of polymer (3 mm) and MRI sequences with a narrow slice selection (1 mm). This allows one to measure local velocities of interstitial flow by reducing the partial volume effects. In the second case, measurements were performed on packed beds with small diameter polymer grains (~ 0.5 mm) and with a wide slice selection (20 mm). This situation provides measurements of averaged interstitial velocity that can be connected to Darcy velocity through maps of porosity. Deviations from 1 % to 5 % are obtained between the flow

rates determined by MRI method and by weighing. Moreover, it is shown that one need to properly calibrate the flow encoding gradient to avoid any phase aliasing inside each voxel of the velocity map.

Finally flow velocity measurements were achieved for packed beds with glass beads, sand and carborundum grains, in order to get closer to real porous media and to take into account the effect of paramagnetic impurities.

P55 Ionic Liquids as Solvent Probes for NMR Cryoporometry

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Ionic liquids (ILs), salts with a melting point below 100 °C, have shown great promise in both experimental and theoretical environments in the past decade. Due to an almost unlimited number of potential combinations of cations and anions, ILs can be tailored to specific applications by adjusting their physical properties. In case of their use as solvent probes for NMR cryoporometry, especially the tunability of the melting point is of great interest.

NMR-Cryoporometry is a non-destructive tool to determine pore size distribution in porous materials in order to characterize catalysts surface. Generally speaking the depression of the melting point of a confined liquid is measured. Coating porous materials with ionic liquids is working very well and is sufficiently known from Supported Ionic Liquid Phase (SILP) catalysis.

The use of ionic liquids as adsorbate shows very promising characteristics. The negligible vapor pressure and the possibility to choose a suitable melting point by varying the ionic liquid offers an easy sample preparation and removes the need for cryogen (as with water or cyclohexane, the most common adsorbates). Furthermore the melting point depression is rather large for ionic liquids. This is due to the high surface energy and the low heat of fusion of ionic liquids compared to water. Therefore ionic liquids offers a wide range of pore sizes measurable, which is larger than those of water or cyclohexane and which covers the measurement range of the most commonly used methods, gas adsorption and Mercury Intrusion Porosimetry.

In this work a calibration curve of the ionic liquid 1-butyl-2-methyl-3-methyl imidazolium trifluoromethylsulfonate [BMMIM][OTf] with several controlled pore glasses is presented. Furthermore the influence on the ionic liquids' melting point after their coating on a support is investigated.

P56 NMR Studies of Fluid Flow within Fractured Porous Media

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Fractures in rocks originate when external forces such as thermal stresses and high fluid pressures place strains on weaken areas. The size of these fractures can vary enormously; they are important to various geotechnical and hydro-

geological engineering processes due to their ability to affect fluid flow via creation of what are effectively local high permeability regions. In this study we ultimately consider various biochemical processes to plug such fractures such that the rock provides impermeable containment of injected fluids.

Traditionally such porous media hydrodynamics are monitored using tracer tests and the resultant breakthrough curves following tracer injection. Here we apply various Nuclear Magnetic Resonance (NMR) techniques to provide both non-invasive and non-intrusive measurements of flow and transport in various porous media with and without fractures. This is predominately achieved using propagator measurements, which are probability distributions of displacement. The non-fractured porous media considered were (i) a 100 micron borosilicate ballotini packing, (ii) Bentheimer sandstone and (iii) Portland carbonate rock. Cylindrical rock cores or bead packings of diameter 37 mm and length 60–70.5 mm were used. All measurements were performed on a horizontal-bore Bruker AV 85 magnet with a magnetic field strength of 2 T. Displacement propagator measurements were performed using the alternating pulsed gradient stimulated echo (APGSTE) [1] pulse sequence as a function of both observation time (0.1 to 2 s) and flowrate using deionised water (7–45 ml/min). These measurements also featured the use of slice selection to avoid contributions from entry effects and non-linear q-space acquisition techniques to improve propagator accuracy. The evolution in propagator shape as a function of either an increasing flowrate or observation time was shown to be sensitive to porous media heterogeneity.

The rock cores were subsequently fractured and the propagator measurements repeated. The change in propagator shape was obvious and can be used as a quantifiable measurement of the extent to which the cracks have been plugged by induced biochemical processes. Preliminary results in this respect will be presented.

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P57 Imaging of Undisturbed Soil Samples by Three Non-Invasive Methods

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The magnetic resonance (MR) imaging and relaxation mapping was conducted on six undisturbed samples of coarse sandy loam from Cambisol series. The same samples were investigated by x-ray computed tomography (CT) and by neutron tomography (NT). Samples were 36 mm in diameter and 100 mm high. Samples were collected in steel sampling tube and then transfered in

quartz glass containers. CT imaging was done at natural field water content of samples mainly to examine the internal structure of the samples. Then each sample was imaged by NT at two different liquid contents, where pore system of four samples contained water (light water) and two samples were filled with mixture of water and deuterium oxide (heavy water). After finalizing the NT measurements, heavy water in two samples was replaced by light water. All samples were then examined in 4.7 T magnetic resonance scanner. MR imaging was done on each sample at least twice with different water contents. MR relaxometry was done on selected samples at high water contents. We found that for soil under study containing light water, with given size of the sample, and current set-up the NT images were obtained only for lowest water contents. This was caused by high attenuation of neutrons in the sample. For samples filled with heavy water we obtained NT images even for fully saturated samples since deuterium attenuates neutrons significantly less than hydrogen. Due to very short T_2 relaxation time water in the soil under study was detected by MR only at high water contents. The results show good qualitative agreement between CT, NT and MRI data. The MRI signal was strongest in regions, where larger pores or voids were detected by CT and where water was also detected by NT. Results of quantitative analysis of data will be given in the poster. The results of the experiment show potential of combining three methods of non-invasive investigation of water phenomena in natural porous media.

P58 Nanoscopically Thin Polymer Films Adsorbed in Porous Metal Oxide Materials: Crossover from Bulk to 2D Dynamics

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Poly(dimethylsiloxane) and poly(butadiene) of different molecular weight have been adsorbed from solution on surfaces of alumina and glass carriers provided as porous media. Employing sufficiently large surface areas, it was possible to investigate, by means of NMR relaxometry and multi-quantum spectroscopy, amounts of polymers corresponding to thin films between less than one and several monolayers. While strong indications for drop-like (i.e. 3D) polymer morphology was found for non-wetting poly(butadiene) but also for PDMS in pores of small radii of curvature (up to 10 nm), the largest pores under investigation, with a radius of curvature of 100 nm, suggested flat (2D) arrangement of polymer molecules. Relaxometry provides evidence for a change in molecular dynamics, in particular a cutoff of Rouse modes for entangled chains, with a layer of typically 1–2 nm thickness near the interface being affected, while the remaining polymer behaves bulk-like in terms of low-frequency molecular reorientation [1,2]. In this region, the Arrhenius temperature dependence vanishes and is replaced by a temperature-activated process of exchange between adsorbed and bulk-like states. The transverse relaxation data, showing nonexponential decays over several orders of magnitude, support this concept and are

in agreement with double-quantum measurements of the adsorbed polymers. Nevertheless, dynamic as well as spatial heterogeneity is observed even for the thinnest layers, which is demonstrated by monitoring the strongly enhanced relaxivity in the presence of surface-adsorbed ferric ions.

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P59 Reaction Monitoring Inside and Outside of Metal-Doped Active Catalyst Pellets by Relaxation and Diffusion Measurements

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Porous catalyst pellets remain one of the most important applications of porous media in Chemical Engineering; they increase reactivity by the presence of a large reactive surface, usually supported by the inclusion of metallic species such as Ni, Pt, Pd, Co, Cu. In order to achieve an optimal reaction efficiency, not only the micropores of these pellets are of relevance but also the macropores and their connectivity across the pellet; often it is only the external fraction of the pellet that takes part in reactions but too small particle sizes would increase flow resistance unnecessarily.

The efficiency of a reactor pellet can be monitored in two ways, either by observing characteristic properties of the pellet interior such as the liquids' relaxation times and diffusion coefficients, or by quantifying the increased mass transport in the exterior volume which is expected from exothermic reactions, but is enhanced significantly more if the reaction involves the generation of gas bubbles.

In this work, the decomposition of hydrogen peroxide, $H_2O_2 \rightarrow H_2O + O_2$, is considered as a standard example for a gas-forming reaction. The decomposition, which is almost absent in the bulk liquid, is considerably enhanced in Cu-, Pt- and Pd-doped commercial Al_2O_3 porous catalyst particles. While distortions of the magnetic field inside the pellets do, in general, not allow chemical resolution and renders imaging difficult due to short relaxation times, it was nevertheless possible to obtain relaxation-weighted images of the interior of Pd-doped pellets that clearly reveal the active region and allow the distinction between environments in the presence and absence of reaction, respectively. The evolution of the reaction over the course of several hours was followed by relaxation parameter imaging in these pellets, and evidence for the influence of pellet packing density on the reaction efficiency is presented. The result of reactions, however, manifests itself in convection outside of the pellet that can easily be picked up by diffusion- or velocity encoding pulse sequences. The average dispersion coefficient in a defined volume represents a measure for the activity of the pellet and/or the remaining reactant concentration. In this study, the

evolution of vertical and horizontal dispersion coefficients was monitored up to the full conversion of a defined amount of H_2O_2, and could be supported by measurements of the transverse relaxation time which is indicative for proton exchange and thus for the remaining reactant concentration. In addition, first results could be acquired for a dedicated hydration reactor that allowed the observation of hexane hydration at a hydrogen pressure of 6 bar and a temperature of approx. 325 K by using a single catalyst pellets. Though the generation of bubbles under these conditions has not yet been confirmed, significant increase in the dispersion coefficients throughout the reaction was observed.

5.4 CMMR 10

P60 Measurement of Compressed Wooden Platelets

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Measuring the proton density of a compressed wooden platelet with the NMR-MOUSE gives important information to the manufacturer concerning different production processes.

The platelets have a thickness of about 6 mm. Using a lift the NMR-MOUSE is able to measure the proton density throughout half the width of the sample. Turning the sample on the other side makes it possible to receive a complete density profile, if both profiles are put together.

The measurement results of the seven different wooden samples show a high proton density towards the edges of the wooden platelet, although the centers of the samples show a low proton density. This means that the density profiles of most samples have the shape of a clinched parabola. A few samples show inhomogeneity concerning the density in the area of the center.

It is concluded, that different types of production processes are responsible for the distribution of the proton density. The distribution is crucial for the firmness of the wooden compressed plates and therefore of interest to the manufacturer to optimize his product.

P61 Simple Single-Sided Mobile NMR Apparatus with a Relatively Homogeneous B_0 Distribution

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We present a single-sided mobile NMR apparatus which generates a relatively homogeneous B_0 distribution and bears a very simple structure. The magnet part of the apparatus only consists of an NdFeB cube magnet (edge length

= 5 cm) and a small NdFeB shim magnet (length = width = 2.4 cm, height = 0.5 cm); both magnets are magnetized in the length direction. The shim magnet is placed directly above the cube magnet; the magnetic axes of the two magnets point in the transverse but opposite directions. In this way, the transverse magnetic flux of the shim magnet partially cancels out that of the cube magnet, creating a region with a relatively homogeneous B_0 distribution above the shim magnet. Notably, the B_0 field is parallel to the magnet surface, enabling the use of a simple loop RF coil [1]. The vertical position of the shim magnet was adjusted such that the profile of the B_0 strength along the vertical axis becomes quite smooth at a point about 6 mm directly above the shim magnet; the B_0 strength therein is about 74.6 mT or 3.18 MHz for ^{1}H frequency. The homogeneous region roughly resembles an upside-down bell [1]. If a maximal B_0 deviation of 2 mT (centered at 74.6 mT) is chosen, the central axis of the bell extends from about 3 mm to 10 mm above the shim magnet; the opening of the bell roughly has an elliptic shape with a major axis length of 12 mm and a minor axis length of 10 mm.

A six-turn circular RF coil (o.d. = 21 mm) was placed about 5 mm above the shim magnet and was tuned to 3.18 MHz; the radius of the RF coil was chosen large enough to excite most of the »bell« region. A copper shield was sandwiched between the magnets and the RF coil to reduce the coil ringing [2]. The magnets and the RF coil were fastened to a polyoxymethylene plastic holder by brass screws; the entire apparatus has a compact structure and weighs only about 1.8 kg. The apparatus was connected to a commercial low-field spectrometer to conduct NMR measurements. The $\frac{\pi}{2} - \tau - \pi - \tau$ - Hahn echo pulse sequence was employed; the $\frac{\pi}{2}$ and the π pulses had equal lengths but different amplitudes. When a 75 W transmitter power is used, the corresponding $\frac{\pi}{2}$ or π pulse length is about 8 μs. Clear echo signals from a pencil eraser, $CuSO_4$-doped water or sewing machine lubricant can be detected in 5 seconds with signal averaging. The T_2 relaxation decays of these samples can be measured by the apparatus using the CPMG sequence; however, the B_0 inhomogeneity results in some diffusive weighting for liquid samples. The maximal detection distance of the apparatus is about 5 mm; 70 % of the signal comes from the 0 mm $< y$(vertical position) < 3 mm region above the RF coil. We will present the detailed characteristics of the apparatus, modifications to enhance the apparatus sensitivity and some applications in the conference.

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P62 **Mobile MRI for In-Line Inspection: Geometry of Rubber Profiles with Sub-Pixel Resolution**

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This work evaluates the performance of mobile MRI for on-line inspection of materials. Particular attention is paid to reconstructing the cross-section of the imaged object with high accuracy and in short experimental times. We show that by applying edge detection algorithms to images acquired with a mobile MRI system, the internal and external contours of the object can be obtained with micrometer precision, surpassing the nominal resolution by more than one order of magnitude. Since the achievable sub-pixel resolution is determined by the signal-to-noise in the image, a tomograph based on a recently optimized compact magnet technology was built for these studies. It is based on a modified Halbach array which generates a high field strength and high homogeneity in a large volume.

P63 **A Unilateral Magnet with an Extended Constant Magnetic Field Gradient**

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Unilateral Magnetic Resonance (UMR) has become, in different research areas, a powerful tool to interrogate samples of arbitrary size. Numerous designs have been suggested in the literature to produce the desired magnetic field distributions. This work presents a new approach which features extended constant magnetic field gradients with a three magnet array. Constant gradients of more than 3 cm extent perpendicular to the magnet surface in a 1 cm diameter cylindrical volume can be achieved in a very simple, compact and safe design. We examine the properties of the constant gradient three magnet array through simulation and experiment.

Diffusion measurements from different positions over the magnet are presented in addition to practical applications for petroleum reservoir core plug characterization within which we measure molecular self diffusion of the saturating fluid, exploiting the extended constant gradient in the sample space. We introduce the idea of a simple solenoidal RF coil encompassing cylindrical samples to aid sensitivity and selective excitation of regions substantially removed from the magnet surface. Simple profiling experiments are also presented.

P64 Unilateral Mobile MR: Novel Magnet Design with a Large Field of View and Adjustability from Homogeneous Field to a Linear Gradient of up to 2 T/m

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Introduction: Mobile Unilateral MR provides the opportunity to scan arbitrarily large or immobile objects. It opens up a wide range of new applications for non invasive in-situ inspection of materials such as tyres or cultural heritage. Two major classes of magnets for Unilateral MR can be found in literature. The first class has field gradients perpendicular to the surface of the magnet. A typical application for this kind of magnets is depth-profiling. The second class offers a remote homogeneous region. This is suitable for imaging or examination of highly diffusive materials [1]. In this work a novel magnet design is demonstrated offering both behaviours with a single setup. It can be adjusted to either have a large homogeneous field of view or a linear gradient that is adjustable over a large range of values.

Materials and Methods: The magnet is built using two NdFeB magnets of $10 \times 4 \times 5\,\text{cm}^3$ with a remanence of 1.4 T. The two magnets are in anti-parallel orientation and connected by a steel yoke of $10 \times 2.5 \times 20\,\text{cm}^3$. This configuration offers a B-Field parallel to the surface of the magnet. In the resulting 10 cm wide gap two diametrically magnetized cylindrical magnets are pivot-mounted (using 4 magnets of $1\,\text{cm} \times 2\,\text{cm}$). The pivot axis of these magnets is 2.2 cm off the centre of the magnet configuration and 1 cm beneath the surface. Depending on the orientation of these cylindrical magnets the field can be adjusted to either offer a large field of view or a linear gradient that can be varied in strength. The cylindrical magnets are divided into two parts for higher order field correction. Three-dimensional field maps were acquired using a hall sensor. These field maps are used to adjust the cylindrical magnets.

Results: In the homogeneous setup the magnet offers a large field of view of $8 \times 6 \times 8\,\text{mm}^3$ with a deviation of less than 3300 ppm. In a reduced field of view of $3 \times 3 \times 4\,\text{mm}^3$ the deviation is less than 500 ppm. The field strength is 108 mT. The field of view has its centre 12 mm above the surface. In the gradient setup the gradient perpendicular to the surface can be varied from 0 T/m to 2 T/m over a region from 8 mm–16 mm ($R = 0.998$). The size of the final setup is $20 \times 6.5 \times 10\,\text{cm}^3$ with a weight of 6.9 kg.

Conclusion: A highly flexible magnet has been built offering both a large field of view in the homogeneous set up as well as a variable linear gradient. It is suitable for unilateral imaging as well as depth profiling.

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P65 A Simple, Compact, and Efficient NMR-Magnet

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A yokeless NMR-magnet is presented. Consisting of 16 identical bar magnets and simple mechanical parts, it can be mounted in a plug and play fashion. The design is derived from the dipolar Halbach array with $n = 4$ identical bar magnets [1] exhibiting high field strength and homogeneity. Omitting the outer halves of the magnets, 70% of the field strength is retained while dividing the weight by two and the cross-section area by four. In practice each half magnet is realized by two magnets with quadratic cross section. Two elements with 4×2 magnets are stacked in order to improve the homogeneity in axial direction. Finite-element simulations show that the homogeneity can even be improved compared to the standard $n = 4$ arrangement by a slight shift of the in-plane distances, realized by distance pieces. The FeNdB-52 bar magnets have handy dimension of 10 mm by 10 mm by 25 mm. Their total volume of 40 ml corresponds to a mass of 300 g. The outer aluminium tube has 45 mm edge length, so the magnet is easily hand held. Samples with 9 mm diameter can be studied. Experimental results for CPMG at 22 MHz are shown. Achieving spectroscopic resolution as with much more elaborated designs [2] is probably unrealistic. However, the magnet is suited for online TD-NMR measurements, provided a NMR pipe of sufficient length for complete polarization is assembled [3]. Given the simple construction and low cost, the setup could also be used for applications requiring disposable magnets. The design can be scaled up to accommodate larger samples and coils for spatial resolution and shimming.

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[3] See also poster: Towards online rheo-TD-NMR of batch polymerization processes, H. Herold, E. H. Hardy, K. H. Wassmer, N. Nestle.

P66 Towards Online Rheo-TD-NMR of Batch Polymerization Processes

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The presented project aims at reliable process analytics by means of rheometry and NMR relaxometry. A compact NMR-based capillary rheometer has been previously realized for close to ambient conditions [1,2]. In order to combine (macroscopic) rheological information with microscopic information on the progress of the polymerization reaction and on dynamic properties of the poly-

mer, Time Domain (TD) NMR is measured at the same time. For studies of »real« polymerization processes, the system is built for operation at elevated temperature and pressure of the liquid flowing through the instrument.

Complex effects occur for relaxometry on samples flowing in inhomogeneous B_0 and B_1 fields (incomplete polarization, inflow, and outflow). For Newtonian liquids and known flow rate, those effects can be calculated analytically and corrected numerically. For non-Newtonian flow, knowledge of the velocity-probability density function (VPDF) is required for the correction of effects.

A flow-through system suited for elevated temperature and pressure has been realized. The probe is equipped with actively shielded gradient coils. A pipe with Halbach-array elements was designed for prepolarization. First experimental results are presented. An outlook on further developments is given.

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P67 Method of Subtraction of the Regular Noise Realized in Hydroscope Device

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Surface Nuclear Magnetic Resonance (SNMR) method is one of geophysical methods that is used for searching groundwater. The main advantage of this method is detection of the resonance signal directly from groundwater molecules. Despite obvious advantages, SNMR has some essential limitations, the main of these is very high sensitivity to electromagnetic interference. This circumstance makes practically impossible the use of SNMR method nearby industrial objects and electrical energy transmission lines. However in the some cases a special methodic allows to essentially reduce regular industrial electromagnetic interference and get positive results of measurement. In this presentation we discuss one of these methods - the method of subtraction of the regular noise realized in Hydroscope device. Hydroscope is an instrument, in which the idea of searching groundwater with SNMR method was realized for the first time. Now it is a device that is actively used in scientific and commercial projects.

P68 On-Line Monitoring of Chemical Reactions in the Fume Hood

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Portable low-field NMR probes built from permanent magnets possess various advantages over conventional NMR systems. They are highly mobile, low in acquisition and operation costs, robust, and are simple to handle. The high flexibility and mobility of low-field NMR systems makes them very attractive for use in industry as they can easily be adapted to meet special demands in different areas of application, e.g. process monitoring of chemical reactions under the fume hood or at the reactor level

The aim of this study was to demonstrate the potential of a newly developed low-field NMR magnet [1] for on-line reaction monitoring. The palm-sized magnet is built from three Halbach rings with different geometric proportions. Each ring consists of an array of eight permanent SmCo magnets with trapezoidal geometry and fixed positions generating parallel gaps between them. These gaps are used to guide small rectangular magnet blocks which are movable radially inwards and outwards to compensate for the inhomogeneities introduced by the imperfections of the pieces. While the central ring generates the main magnetic field, the displacement of the two outer rings along the z-axis can be varied to shim the field along the axial direction. Field distortions along the cylinder axis due to the finite magnet length can be minimized in this way.

As a model reaction, the trimerization of propionaldehyde under environmentally advantageous solvent-free conditions was chosen. The reaction was monitored on-line using ^{1}H NMR spectroscopy by continuously circulating the reacting liquid through the NMR magnet. The reaction has been conducted directly under the fume hood and with standard lab equipment. The progress of the reaction has been recorded with high temporal resolution for two different catalysts. High-field NMR control experiments were in good agreement with the results obtained with the new low-field NMR magnet.

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P69 Characterization of Complex Products by a Single Sided NMR Instrument

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There is a wide potential application of single-sided NMR devices in industrial projects. The systems become particularly interesting, because of their unique capability to be transported without inconvenience in several environments. The application and usefulness in cultural heritage studies (e.g. paintings, paper and ancient walls) and in surface material analysis (e.g. polymers, tires) is very well

known [1]. In principle they could be also usefully employed in a wide range of industrial process monitoring (including large manufactured products in general) and in testing construction materials. Data acquired by single-sided NMR devices usually suffer from artifacts owing to their highly inhomogeneous B_0 and B_1 magnetic fields. A comparison between results of parallel studies performed by means of single-sided and benchtop instruments can help to better know the limits of mobile instruments and eventually to correct data. In this study we have investigated the possibility of getting quantitative NMR measurements on products derived from complex oil and petrochemical industrial processing and manufacturing. The purpose is to improve knowledge of chemical and physical properties with a fast and reasonably mobile technique. Highly viscous products, such as hydrocarbon deposits and bitumens, characterized by very short T_2 values due to the low mobility and the presence of a dispersed fraction of solid particles in the viscous matrix were considered. Measurements were acquired on the same samples in the highly homogeneous magnetic field of a standard benchtop NMR instrument and in the inhomogeneous fields of a mobile device. The comparison of the signal response from the two instruments are discussed regarding the possibility to obtain quantitative interpretations of the data.

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P70 Measuring High Resolution Skin Profiles with Optimum Contrast by Portable One-Sided NMR

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MRI is routinely used to generate tissue-specific contrast in images of living species. Nevertheless, images with the resolution required to resolve the stratigraphy of skin are hard to obtain with conventional MRI machines. This spatial resolution can be easily obtained working on the strong gradient of the stray field generated by portable single-sided NMR sensors. The Profile NMR-MOUSE© [1], for example, selects a sensitive slice that can be swept along the depth direction to measure depth profiles with a resolution better than $5\,\mu m$, and up to depths of about $10\,mm$ into the sample.

In the presented work a procedure for setting the optimum contrast between any arbitrarily chosen subset of skin layers is shown. In order to independently evaluate the effect of each contrast parameters, skin profiles of the thenar were measured on 3 volunteers with $50\,\mu m$ resolution up to $1200\,\mu m$ depth with the Profile NMR-MOUSE©. T_1 was measured with the saturation recovery pulse sequence, T_2 was obtained from a CPMG experiment, and the diffusion coefficient was gained from the STE-pulse sequence. From each data set a 2 component behavior was extracted by numerical fitting. The profiles reveal sections with characteristic ranges of parameters by which the skin layers can be distinguished. Knowing the influence of the characteristic T_1, T_2, and D values of each layer, allowed us to maximize the contrast in the profile by properly setting

the recycle delay, number of echoes, and echo time of the CPMG sequence used for signal detection.

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P71 Ultra-Compact MRI

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We have been working with small, dipolar NMR magnets that create strong, very homogeneous fields over small working volumes. These magnets are a good size match to the millimeter-scale coils we use; they are also simple and inexpensive to build. The magnets have allowed us to demonstrate an easily portable ultracompact NMR spectroscopy system. Recent efforts have resulted in an improved magnet system: the field has increased from $1\,\mathrm{T}$ to $1.7\,\mathrm{T}$ and first and second order shim coils allow the field to be shimmed to better than 25 parts per billion (for small coils) on a routine basis. In addition, careful positioning of the coil in the sweet spot is no longer required to achieve high resolution.

The improved magnet is well-equipped for MRI. The small linear shim coils produce relatively strong gradients while having negligible inductance. We have constructed a simple low-power current-feedback amplifier that is adequate for controlling both shimming currents and the pulsed imaging gradients. To supply the pulsed gradient waveforms, we use a commercial digital I/O board (Spincore) to drive a 4-channel digital-to-analog converter chip (Linear, LTC2755). The gradient control and amplifier are very compact and the entire prototype MRI device, including magnet, is roughly the size of a standard desktop computer enclosure.

The system is in the early stages of development; its current performance will be discussed in this presentation. The system is obviously limited to imaging very small objects. One such object is the Xenopus lavis (frog) embryo, which is an important organism in developmental biology research. The embryo begins as a single cell, roughly $1\,\mathrm{mm}$ in diameter, and initially grows by subdivision without changing size substantially. High field MRI has been applied in studying embryonic development in real time, but only a few groups in the world have access to the instrumentation required. An ultracompact MRI system of reasonable cost would dramatically increase the role of MRI in the field of developmental biology.

P72 Unilateral NMR Study of Fat Stains on Textiles During Simulated Washing Processes

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Profiling studies by unilateral NMR provide a unique possibility to study the impact of washing formulations on fat-stained tissues. Experiments were carried out on a thermally stabilized ACT profiler with a measuring depth of 5 mm in a specially designed flow-cell and fat-stained pieces of cotton rags. Depth resolutions of about 50 µm could be achieved within measurement times of about 20 min. When reducing the number of slices, the measuring time can be reduced to less than 1 min.

Contrasting of fat and water was achieved by combined T_1 weighting and diffusion weighting in the intrinsic background gradient of the NMR profiling device. The influence of the water flow inside the cell on the observed contrast was studied, too.

The results indicate that various processes occurring during the washing process can be identified in the NMR experiment: swelling of the fat due to uptake of tensides, removal of fat by emulsification and changes in the mobility of the fat phase due to selective removal of certain components of the fat.

P73 Morphology of Polyethylene Pipes Across the Wall: A Combined Low and High Field NMR Study

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Polyethylene is one of the most important materials in our daily lives; since decades it is wildly applied for pipe systems used for the transport of gas, liquid, and sewer. The standardized life time of this material is supposed to be 50–100 years under normal operation conditions. However, the real service time is influenced by different factors, such as the initial resins, the processing parameters, and the local conditions under service. Therefore, in order to be able to prolong their service life, characterization of these materials at microscopic level, with the help of proper analytical methods, has to be done. However, for most techniques, the samples have to be send into the lab and cut into small pieces before investigation which makes the study of the pipes under service impossible. To this end, nondestructive testing methods are needed to obtain morphological information about the pipe material. Solid state NMR is our days a well established analytical tool able to provide structural, dynamical, and morphological information. Moreover, relaxometry measurements performed using unilateral NMR systems such as the NMR-MOUSE represent a truly non-destructive way of accessing details about the polymer morphology.

During the processing, the plastic pipes are cooled down mainly from one side so that different layers across the wall of the pipe undergo different thermal

history. This leads to the formation of a morphological gradient across the wall which is expected to influence the life time of the pipes. However, up to now mainly no information about this morphological gradient is available. Therefore, our study deals with the influence of the manufacturing conditions on the morphology of the pipe across the wall at microscopic level. This was done by using the advantages offered by unilateral NMR systems such as the Profile-NMR-MOUSE. Further on, a correlation of the results obtained from the relaxation data with the NMR-MOUSE with those estimated by high field NMR was done.

P74 Low Field Portable NMR Studies of Wilting Leaves

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Non-spatially resolved portable NMR is becoming available to study leaf water content (LWC) and distribution of water in different (sub-cellular) compartments, e.g. chloroplasts. These parameters directly relate to plant transpiration, CO_2 uptake, and photosynthesis. Application of portable NMR is not straightforward due to magnetic field inhomogeneities, complex leaf structure and shrinking-elongation movements during changes in LWC. Here we investigate the quantitative relation between LWC and NMR signal intensity as observed by a surface coil.

The dehydration of leaves of different plants was studied continuously from the moment they were removed from the plant until their mass became constant. Two approaches were applied to follow the wilting process in leaves. One was to use portable NMR while the second was a simple weighing method until the sample has been dried out completely. The NMR signal was obtained by Carr-Purcell-Meiboom-Gill (CPMG) sequence for determination of the spin-spin relaxation time using two magnet systems with a homogeneous magnetic field (10 MHz) and with a very strong static magnetic field gradient (18 MHz, 20 T/m) in combination with a surface coil.

For the first time we monitored changes in water status of a whole leaf, directly correlated to weight measurements. The NMR results were compared with changes in LWC. The results demonstrate that the NMR signal is uniquely and quantitatively related to LWC, in contrast to observations reported elsewhere.

P75 Low Noise RF-Frontend with Flexible Microcoils for Mobile NMR Applications

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An analog frontend for mobile NMR spectrometers is presented that is specifically designed for flexible microcoils. The whole circuit is intended to be used with the open MOUSE(TM) magnet to perform single-sided NMR experiments.

It consists of planar micro structured coils, an adjustable tuning circuit and active amplification stages. It is carefully laid out to achieve the smallest possible overall noise figure (NF).

The micro structured coils were each fabricated on flexible polyimide tapes with a total thickness of less than $50\,\mu m$. They were optimized to analyze small films of larger objects by completely simulating and measuring their electrical parameters and magnetic field components with high accuracy. As an example a rectangular coil with 10 windings, an inner edge length of $2.5\,mm$ and conductors of $100\,\mu m$ width and $50\,\mu m$ spacing was constructed to analyze a sensitive area of about $7\,mm^2$ at an optimal distance of $0.5\,mm$.

To tune the coils to the Larmor frequency of the used $0.4\,T$ magnet a parallel resonant circuit was built with fixed capacitors and varactor diodes utilizing non-magnetic and high-Q components. The varactor diodes allow for fine-tuning of the resonance frequency to account for changes due to probe influences and possible deformations of the flexible coils. Furthermore, the circuit can thus be actively de-tuned to minimize the coupling between the receiving microcoils and a separate excitation coil. The tuning circuit shows a high Q-factor of 25 at $17\,MHz$ with the above-mentioned coil and its degradation due to the varactor diodes is negligible.

To maintain a high signal-to-noise ratio a new technique is used exploiting the passive voltage amplification of the resonant circuit itself formed by the coil and the parallel tuning capacitance. In this way both the signal and noise voltages induced in the receiving coil are boosted by a factor equal to the circuit's Q-factor. Most importantly this noiseless amplification takes place previous to the subsequent active amplification stage. Using this technique the noise voltage of the coil is increased to a level beyond the input referred noise voltage of the active amplifier. Consequently the contribution of this amplifier to the receiver noise and likewise the total NF is minimized. Although this technique is superior to the common $50\,\Omega$ power matching scheme it is reported only once in combination with NMR spectrometers up to now.

The passive amplification is maximized by using both high-Q micro coils and an ultra-low noise operational amplifier with a high input impedance. This results in an overall NF of less than $0.3\,dB$ whereas commercial low-noise $50\,\Omega$ preamplifiers are limited to values of about $1.0\,dB$ in the frequency region of interest. The necessary tuning and amplification circuits were assembled with only a few highly miniaturized components forming a very compact and low-noise frontend design that is ideally suited for mobile NMR.

5.5 Hyperpolarization

P76 Capillary Blood-Flow Analysis by Continuously Dissolved Hyperpolarized ^{129}Xe and ^{1}H Velocity MRI

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NMR as a non-invasive analysis tool is well suited for studying the complex flow behavior and resulting physio-chemical changes of blood in vivo as well as in vitro. Especially for medical engineering, the mechanical stress which leads to destruction of red blood cells (RBCs) in regions of high shear stress has not yet been understood completely and needs to be observed in situ [1]. Optical methods yield only indirect results as a consequence of the opaqueness of blood. ^{1}H NMR velocity imaging has proven to be feasible for studying general blood flow behavior [2]. However, it does not allow differentiation between different physical or chemical surroundings, e.g. plasma and RBCs. Because of the large electron clouds of xenon atoms, ^{129}Xe NMR provides a very sensitive chemical shift and thus can provide important additional information. In order to enhance the intrinsically low signal achievable with this artificially administered sensor nucleus, hyperpolarization (HP) as well as the so-called xenonizer technique of continuously dissolving HP ^{129}Xe into a fluid via hollow fiber membranes have been employed [3,4]. Thereby, images of capillaries with inner diameters of 500–750 μm containing blood model fluids, porcine plasma, and whole blood could be acquired while important chemical shift information was maintained. The comparison of both, spectroscopic HP ^{129}Xe imaging and ^{1}H velocity MRI serves as the basis for further studies in more complex geometries to improve clinically relevant appliances such as artificial lungs, blood pumps, dialyzers, and many more. Furthermore, in the future, this method could also prove feasible for in vivo blood flow measurements in large blood vessels down to fine blood capillaries.

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P77 A Complete Platform for PHIP Method

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In recent years many efforts have been devoted to the development of MR-

hyperpolarization methods. Parahydrogen-Induced Polarization (PHIP) is an efficient technique that permits to overcome the low sensitivity problem of NMR spectroscopy and to increase the wideness of Nuclear Magnetic Resonance (NMR) experiments and applications. The PHIP method allows to achieve high polarization percentages in very short time. In this work we present some results obtained by a complete platform for PHIP that allowed us to reach up to 30% ^{13}C nuclear spin polarization. The PHIP polarizer used combines an improved para-hydrogenation reactor with a highly reliable pulse programmer (Stelar srl, Mede PV) for polarization transfer at low magnetic field. A double-tuned RF circuit operating at $2.27\,\text{MHz}$ (^{1}H) and $0.57\,\text{MHz}$ (^{13}C) allows RF transmission of a pulse sequence acting on ^{1}H and ^{13}C to turn the antiphase ^{13}C signal into net magnetization. The correct application of the pulse sequence requires the accurate calibration of ^{1}H and ^{13}C pulses. In particular the ^{13}C pulse calibration was obtained using an on-purpose Field Cycling method. The results with high reproducibility are presented in the poster

P78 Nuclear Magnetization as a Field

Stanislav Sykora[1]
[1] Extra Byte

The routine practice of NMR in any of its many forms consists in creating a non-equilibrium nuclear magnetization and then tracking its evolution in time. In homogeneous samples, the evolution can be described by simple equations which can be of quantum, classical, or semi-empirical nature (such as Bloch equations). Whichever the case, the description of magnetization evolution in a homogeneous sample does not require the use of macroscopic space coordinates, while the situation is different in heterogeneous samples. Here various parts of the sample exhibit different MR properties; consequently, magnetization can travel across the sample by means of material convection and diffusion, chemical exchange, spin diffusion and collisions and it can return to its thermal equilibrium preferentially at space locations where relaxation is particularly fast (relaxation centers), giving rise to a new set of NMR phenomena.

Mathematically, the situation is reminiscent of field theories such as the classical heat theory. We see an analogy between heat and magnetization (extensive properties), temperature and polarization (intensive properties) and between heat capacity and density of nuclides (material properties). One can also define material properties such as magnetization conductivity, akin to thermal conductivity. Differences consist mostly in the fact that magnetization and polarization are vector quantities rather than scalars and, due to the applied magnetic field, they evolve in an axially asymmetric environment. Another difference consists in the non-conservative nature of the magnetization due to relaxation. While heat is conserved and sample temperature just equilibrates, magnetization and polarization of every sample voxel return spontaneously to pre-defined values. In addition, each kind of nuclides (or electrons) defines its own magnetization

field and several such fields may be co-present in a sample and be mutually coupled.

This presentation proposes phenomenological equations of a spin magnetization (SM) field theory encompassing the known static and dynamic aspects of longitudinal spin magnetization in heterogeneous samples. The purpose is to open a critical discussion and stimulate experimental verification. It is also hoped that the formulation could stimulate novel experimental techniques for the study of magnetization transport phenomena. The SM field equations lead to a more realistic description of relaxation phenomena in porous samples, suspensions, emulsions, solutions of macromolecules and micelles, bacterial broths, cellular tissues, etc - all systems where relaxation occurs predominantly in a limited fraction of the sample volume. Consequently, the evolution of the detectable NMR signals, is often affected principally by a limited number of local relaxation mechanisms and by the characteristics of magnetization transport from other parts of the sample to these local magnetization sinks.

5.6 Novel Techniques, Pulse Sequences, and Spin Dynamics

$\boxed{\text{P79}}$ **Entangled and Liquid-Like Chain Discrimination on Model Polymer Networks Studied by Double Quantum - CPMG Based Sequences**

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A variety of systems is characterized by having both solid-like and liquid-like behaviors that can be often individualized by relaxation experiments, as for example by using a CPMG sequence. An alternative method that is commonly used is the measurement of creation and evolution of multiple quantum coherences (MQC). By monitoring the build up and evolution of the different MQC a great deal of information ranging from cluster sizes, connectivity, and decoherence processes can be obtained [1,2]. In this work we present an approach based on an encoding period with MQC and a detection one with a CPMG pulse sequence. Very well characterized model PDMS polymer networks are used to test the performance of the proposed method.

Double-quantum (DQ) spectroscopy has repeatedly been recognized as a uniquely selective tool for the determination of residual couplings in polymeric systems. Cross-linked elastomers exhibit both liquid-like and solid-like features. At temperatures well above the glass transition temperature, the time scales of molecular motion are liquid-like. However, the presence of permanent cross links and topological constraints prevents the chain motion from being isotropic.

Thus, anisotropic spin interactions such as dipolar interactions are not completely averaged out and give rise to solid-like NMR properties [3,4].

On the other hand, relaxation of transverse magnetization is mainly determined by the dipole-dipole magnetic interaction between protons. This interaction is modulated at different extents by molecular motions and is sensitive to differences in the motion of the chains that form the polymer network. This technique is very precise to measure the ratio between the entangled chains that form the network and the pendant material [5].

In this work we combine both methods in order to obtain the very reliable information of dipolar couplings obtained by DQ-NMR while the influence of liquid-like material is removed by direct inspection of the signal detected by a CPMG pulse sequence. If an additional DQ encoding period with a duration fixed at the maximum of the DQ build up curve, a filtering of the signals that comes from the liquid like segments is produced. Monitoring the evolution of the signals with the CPMG sequence can render information on spin-diffusion from entangled chains to pendant material.

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P80 Performance of Two-Sequence, Two-Inversion Pulse PERFIDI Filters to Suppress and/or Quantify Relaxation Time Components in Multicomponent Systems

Villiam Bortolotti[1], *Paola Fantazzini*[1], *Mirko Gombia*[1], *Danilo Greco*[2], *Giuseppe Rinaldin*[1], *Stanislav Sykora*[3]
[1] University of Bologna, [2] Esaote S.p.A., [3] Extra Byte

Many of the natural and artificial systems analyzed by ^{1}H-NMR/MRI present populations of nuclei contributing to the signals with distributions of T_1 and T_2 relaxation times. When working with such systems it can be useful to quantify and/or suppress relaxation time components. Examples are the suppression of fat to improve MRI contrast in tissues, the evaluation of the fat-to-lean ratio in the meat, or the separation of signals from water and oil in porous rocks. A common practice to suppress components is to exploit the differences of T_1 (the standard sequences following this approach are STIR, MIR and DIR).

The method called Parametrically Enabled Relaxation Filters with Double and Multiple Inversion (PERFIDI) [1-3] is based on a different line of reasoning:

its effect is not to exactly zero the signals for a discrete number of T_1 values, but to strongly attenuate the signal in selected ranges of T_1 values, while the remaining signals are affected by a computable attenuation, in analogy to the electronic band-pass, high-pass or low-pass filters, emphasizing primarily the components which pass through, rather than those which are blocked. PERFIDI filters are used to separate the sample components according to their T_1 values prior to data acquisition rather than doing it mathematically a-posteriori and is particularly useful when a continuous distribution of T_1 values is expected. The PERFIDI protocol consists in the acquisition of signals from a chosen rf pulse sequence combined with two or more PERFIDI preambles, and combining linearly the acquired data sets. Each pulse sequence is thus made of two parts. The first one is the preamble, made of a series of inversion pulses, whose timing is varied depending on the desired filter behavior. The second one is the conventional rf sequence to which the filter is applied.

In this presentation we investigate the performance of a PERFIDI protocol based on two-sequences with two-inversion pulses. It is particularly useful in the presence of samples with bimodal distributions of longitudinal relaxation times. Based on the PERFIDI method, we have developed a protocol for very fast determination of the ratio between fat signal and total signal, avoiding the time consuming Inversion-Recovery data acquisition, and applied it to biological samples containing fat. The same method was implemented on ARTOSCAN tomograph (Esaote S.p.A., Genoa, Italy), providing well T_1-contrasted images.

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P81 Recovery of Noise-Corrupted NMR Data Acquired and Accumulated in Unstable Magnetic Field

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During the acquisition of NMR signals in unstable magnetic field conditions, the in-phase and in-quadrature signals I & Q cannot be cumulated to improve SNR. On the contrary the modulus S is not affected by B_0 field instability. Nevertheless the modulus of a NMR signal can be cumulated in unstable magnetic field but this operation introduces an error called noise bias which is due to the rectification of noise. An algorithm and a method to estimate noise bias and subtract the related errors has been described in a previous poster by authors. Objective of work presented is to test the applicability and the effectiveness of the correction method applied to real NMR data acquired in unstable field for

the estimation of T_1 and T_2, in particular in NMR Fast Field Cycling where field stability is the main limitation for the acquisition of T_2 data. The NMR signals of all the experiments have been acquired and accumulated point by point in the I(real), Q(Imaginary) and S(modulus) components, exploiting a particular capability of the Stelar PC-NMR console which allows the parallel accumulation of data both in Cartesian and polar coordinates.

The noise bias error is estimated and directly used to correct original NMR data. The T_1 and T_2 data have been acquired with different number of scans both in stable and unstable field using Inversion Recovery, Saturation Recovery and Spin Echo experiment. The values of T_1 and T_2 have been fitted using Cumulated Modulus, Cumulated and Corrected Modulus and Calculated Modulus from the accumulated I and Q signals. All results are presented and discussed in the present poster.

Conclusions: The results of measurements done both in stable and unstable field demonstrate that the modulus of an NMR signal can be cumulated, corrected and used for the estimation of relaxation time T_1 and T_2.

P82 A Fast Algorithm for Computing the Pulsed-Gradient Spin-Echo Signal in Multiscale Porous Media

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A reliable interpretation of pulsed-gradient spin-echo (PGSE) experiments in mineral samples and biological structures such as concrete, sedimentary rocks or lungs, requires intensive numerical studies of restricted diffusion [1-4]. Classical Monte Carlo simulations with a fixed time step are too long and inefficient in such porous media [5]. I propose a fast algorithm for computing the PGSE signal in multiscale structures. The algorithm relies on random walks with variable jumps which are adapted to local geometrical length scales [6-8]. An implementation of gradient encoding is a new feature that opens a possibility for efficient and accurate numerical simulations in model and reconstructed three-dimensional porous media.

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P83 Rapid Gradient Switching for MR/MRI

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[1] University of New Brunswick - MRI Centre, [2] University of New Brunswick - Physics Department

Eddy current effects on a magnetic field due to pulsed magnetic field gradients are normally corrected by a pre-emphasis network to shape the currents supplied to the gradient coils. These adjustments are often made empirically and iteratively. With traditional pre-emphasis gradient slew rates are still limited by the gradient coil self-inductance.

We propose a new digital waveform pre-adjustment method. The method is guided by MFGM [1] measurement of gradient waveforms but the correction required is predicted by theory. Eddy currents were modeled by lumped RL circuits. For a desired output waveform, the required new input waveform may be calculated through Laplace transformation manipulations based on a simple circuit model. Compared to previous pre-emphasis work, the new method, demand compensation waveform adjustment, combats self-inductance of the gradient coil or high mutual inductance (e.g. eddy currents) by adjusting the gradient voltage at the cost of using a more powerful gradient driver.

This strategy is applied, for the first time, to rapid switching magnetic field gradients with highly conductive metal structures present. The presence of metal vessels results in a high mutual inductance between the gradient coil and the metal. It is known that gradient switching time is proportional to the load inductance. A mock metallic pressure vessel [2,3] fabricated using aluminum was employed. The MFGM [1] measurement shows that the gradient rise time (from 10 to 90 %) was 10 ms in the presence of the metal vessel. The pre-adjusted waveform was calculated based on the proposed algorithm. After adjustment, the output gradient waveforms were measured again. The results for two cases show that the gradient switching time was reduced by a factor of 2 and 3.5 respectively. The gradient waveform decay after gradient turnoff with adjustment is still exponential but with its time constant significantly reduced.

The benefits of the demand compensation adjustment we anticipate will be very general. The idea will be applied to reducing TE in a variety of pulse sequences in conjunction with MRI inside metal vessels [2,3]. The method also has potential to improve gradient performance in a variety of clinical MRI pulse sequences. In general we favor direct adjustment and improvement of magnetic field gradient performance rather than employing knowledge of non-ideal gradient waveforms for data post processing.

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[3] H. Han et al., J. Magn. Reson. accepted.

P84 Low Gradient Diffusion Editing

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Motivation: Obtaining diffusion measurements in a low gradient field has been typically considered too difficult to do due to a lack of diffusion encoding. The standard double echo diffusion encoding sequence (DEc-DE) is routinely run as a pulsed field gradient (PFG) sequence with gradient values typically from 3 G/cm to 48 G/cm. The aim of this work was to develop a sequence for use in a low constant gradient field such as that found in some downhole oilfield logging tools.

Theory: The diffusion editing technique is now a well established technique used to discriminate fluid types through the use of both T_2 and Diffusion coefficient information. In the standard DEc-DE PFG sequence a series of experiments are repeated with varying gradient strengths and a diffusion distribution is obtained. By adding a CPMG to the end of a diffusion encoding sequence one can also obtain the T_2 distribution. By then doing a 2D Inverse-Laplace transform a 2D map is generated to provide a graphical representation of the fluids contained within the sample such as oil and water in an emulsion or a hydrocarbon bearing formation. In the new single echo diffusion encoding sequence (SEc-DE) with a constant gradient, we vary the diffusion encoding time in a series of experiments in order to extract the diffusion encoding information. The use of the SEc-DE sequence increases the diffusion encoding time by ~ 4. This helps to offset the reduction of the gradient on the diffusion.

The performance of this sequence was compared to the standard DEc-DE PFG with respect to the ranges of fluids that can be characterized. At low gradient strengths the encoding times have to be increased to allow for more diffusion. The maximum required values were theoretically calculated and can be done for each gradient strength. For T_2 values above the cutoff value, the encoding times for optimal sensitivities for SEc-DE can be easily approximated and it has been shown that the single echo significantly improves the T_2 and D cutoff compared to a double echo sequence.

Results: Results from the two different sequences obtained from a Maran 2 MHz system on a mayonnaise sample. It was found that the water cutoff values range for SEc-DE from about 7 ms for 30 G/cm, to 36 ms for 3 G/cm. The corresponding oil cutoff values for SEc-DE range from about 40 ms for 30 G/cm to 122 ms for 3 G/cm. At 30 G/cm, oils with a viscosity up to about 40 cP can be fully characterized, - at 3 G/cm the oil viscosity must be below 13 cP.

Conclusions: Single-echo DE has a higher diffusion sensitivity than standard double echo-DE. Quantitatively, the T_2 cutoff for water for single echo DE is reduced by a factor of 1.6 compared with that for double echo DE, and the T_2-cutoff for oil is reduced by a factor of 1.4. Correspondingly, the range of viscosities for oils that can be fully characterized with DE is increased by 40 % with single echo encoded DE compared to double echo DE.

P85 Acoustically Stimulated Magnetic Field Gradient NMR: a New Characterization Method for Determination of Fluid Transport Properties in Porous Media

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We discuss a recently developed approach for determining flow permeability using NMR with magnetic field gradient measurements in the presence of induced oscillatory fluid flow. The concept is to measure the local velocity of fluid in the pore space of a porous media using magnetic field gradient NMR where the local motion of the fluid is created in response to an externally applied time varying pressure. If the fluid in the porous media is in hydraulic contact with the external fluid source the local pressure in the pore space can be transmitted from a remote acoustic source. Pressure could be applied at the surface of a drill well and transmitted by the borehole fluid to the formation of interest. The time varying mechanical stress at the formation boundary generates a fast compressional wave that propagates through the formation, and generates an oscillatory displacement of the formation matrix together with the formation fluid. Biot theory relates the relative fluid flow, which controls the permeability, to the motion of the formation matrix.

With the acoustic-NMR technique the distribution of fluid velocities within pores and the distribution of pore sizes can be probed. The relative local fluid motion in the formation pore space is measured using field gradient space coding techniques with simple spin- or stimulated- echo sequences. Such measurements are possible using the current generation of commercially available bench top NMR systems and potentially in down hole logging tools. In 2008 we completed the construction of a laboratory acoustic-NMR prototype unit for experimental verification of recently developed theory and to determine limitations of the technique for laboratory and downhole applications. This presentation will focus on several experimental approaches that we have identified to measure acoustically induced molecular displacement and flow velocity in a porous matrix. 2D CPMG with constant magnetic field gradients is the simplest, least hardware intensive, and therefore most promising experimental protocol that provides precise information on molecular displacements resulting from oscillatory motion. Other protocols with pulsed field gradient (PFG) provide more detailed information about fluid motion, but are more hardware intensive. For example, analysis of real and imaginary signals of the PFG spin-echo response

to coherent acoustically induced oscillatory flow simultaneously provides both self-diffusion and flow distributions of fluid within the porous matrix.

P86 Monitoring Ultrasound Processes of Crude Oil Products by Low Field NMR

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The correlation between ^{1}H NMR relaxation times or diffusion coefficients and viscosity is very well known and often applied in the characterization of materials [1]. These methods could be effectively implemented on standard benchtop NMR spectrometers and applied to the study of industrial processes both off-line and on-line. NMR pulsed field gradient diffusion experiments, relaxation times and hydrogen content measurements were applied to collect information on the viscosity of crude oils coming from different reservoirs. The results were compared with rheological and chemical parameters obtained by standard ASTM methods. Moreover, the methods were applied in studying the variation of viscosity in crude oils determined by chemical and physical treatments.

The viscosity determination was particularly useful especially for the possibility of applying the method to heavy oils (characterized by the presence of suspended solid particles), without manipulating the products. In such a case, a careful calibration of dynamic viscosity values with a standard rheological method is needed. The great advantages involved in the NMR technique application, are mainly the fast estimation of viscosity even for complex materials and the possibility of monitoring the processes while occurring and without any appreciable interference. In our case we have performed the measurements based substantially on standard CPMG sequence, during Ultrasonic (US) irradiation of a heavy oil product. The data acquired during irradiation of the heavy oil products indicated an appreciable reversible viscosity reduction during the treatment [2].

The viscosity features of the samples were then substantially recovered at the end of the experiment.This is probably related to the effect of a mechanical stimulation on the colloidal nature of the products under US irradiation. The experimental data demonstrate the feasible application of such methods on a large range of samples, providing an efficient and fast method suitable to be applied directly on the industrial site.

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P87 Gigapascal NMR: A Novel Approach to Nuclear Magnetic Resonance at High Pressures in Anvil Cells

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Pressures well into the gigapascal range are routinely achieved in so-called anvil cells but limited sample size and anvil cell geometry hampered their use in nuclear magnetic resonance experiments due to a weak signal-to-noise ratio. Here we report on a novel approach that places the radio-frequency coil inside the high-pressure region resulting in an increased filling factor of the coil and thus improving sensitivity significantly. We also show first high-sensitivity measurements on metallic aluminum at pressures up to 7 GPa.

P88 QT Inversion of Surface NMR data

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The technique of surface nuclear magnetic resonance (surface NMR) is the only geophysical exploration method providing direct and nondestructive information on subsurface aquifer properties due to the method's unique sensitivity on hydrogen protons. The method combines the information content accessible via nuclear magnetic resonance (NMR) measurements and the nondestructive approach to derive subsurface information from surface-based measurements. Because of this, surface NMR became a useful tool for hydrogeophysics during the last decade.

Surface NMR adopts the principles of NMR measurements by emitting the excitation pulse and recording the relaxation signals (free induction decays - FID) using large surface coils. In contrast to laboratory NMR, that places a sample inside a strong artificial primary magnetic field, the object of investigation is outside the loop and the earth field acts as primary field. The electromagnetic wave propagation of both, the excitation field emitted by the surface loop and the relaxation signal originating from the illuminated subsurface volume, determines the spatial location and measurability of the NMR signal. Consequently, the spatial sensitivity is based on changed excitation intensities q, that are products of the loops current and duration of the excitation field. Thus, surface NMR datasets are NMR signals in dependency of the pulse moment q. Furthermore, surface NMR data is complex valued, both due to the subsurface resistivity and possibly separated loops for transmitting the excitation field and receiving the FID's. In the most simple 1D configuration surface NMR is referred to as Magnetic Resonance Sounding (MRS) and operates with a single loop at the Earth's surface.

Currently, two different inversion schemes exist to solve the ill-posed MRS inverse problem, i.e., estimating water content and decay time depth distribution from the measured surface NMR dataset. The initial value inversion (IVI)

extracts the water content depth distribution from the surface NMR dataset by estimating a sounding curve from surface NMR data. The time step inversion (TSI) extracts the distribution of both water content and decay time by separating the surface NMR data into several time steps. Both solve the inverse problem using independent steps and by separating subdatasets from the complete data.

A new inversion scheme - the QT inversion (QTI) - is found to solve to inverse problems by taking the complete surface NMR dataset into account at once. QTI extracts water content and decay time and satisfies the complete dataset jointly. We examine and compare QTI to IVI and TSI by a synthetic dataset and a field dataset. Our results find that the QT inversion approach increases both spatial resolution of the subsurface decay time distribution and stability of the inverse problem.

P89 Ultrafast Velocity Mapping in Planar Micro-Structures

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NMR has proven to be a powerful tool for the characterization of flow in microfluidic setups like lab-on-a-chip mixers or reactors [1-4]. Such devices contain planar arrays of microscopic channels and chambers that need optimization to maximize throughput. So far, the full potential of NMR to monitor the flow pattern inside these structures has not been reached. Various obstacles, e.g. B_0-inhomogeneities generated by the micro-structures, B_1-inhomogeneities imposed by the use of designated surface rf coils and the high flow velocities in micro-devices, have prevented the implementation of ultra-fast velocity mapping techniques based on multi-echo generation. In this work, we exploit the advantages of the FLIESSEN pulse sequence [5] (FLow Imaging Employing a Single Shot ENcoding). It is a combination of an ultrafast RARE-based acquisition with frequent updates of velocity-encoding and exhibits a high resilience to the above-mentioned inhomogeneity and high-velocity effects, while simultaneously allowing high spatial and temporal resolution. The performance of this technique is demonstrated on a phantom that bears all characteristics of a micro-device. Using a planar surface rf coil in combination with the FLIESSEN pulse sequence, high-fidelity 2D velocity maps were obtained within seconds.

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P90 **Two-Dimensional T_2 Mapping with Phase Encode MRI for Core Analysis**

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We have presented two phase encode MRI sequences for measuring spatially resolved T_2 distributions in 2-D. Following our previous work on 1-D versions of the sequences [1], we explore two different approaches to T_2 mapping: in one sequence, the T_2-weighting precedes the spatial encoding (scheme A), and in the other, the T_2-weighting follows the spatial encoding (scheme B). A spiral SPRITE pulse sequence with a CPMG-prepared magnetization has been chosen for scheme A. To remove a steady-state component of the SPRITE signal, the prepared magnetization is stored alternately along plus and minus z-axis, afterwards a difference signal is acquired. Scheme B is realized by extending our previous 1-D spin-echo SPI sequence [1] onto 2-D, by merely adding the second phase encode gradient. In this sequence, the magnetization is phase encoded within the first pulse interval and then read out through multiple refocusing under XY-16 phase cycle. To avoid a N-fold increase in the number of scans upon the extension from 1-D to 2-D, we employ one of the scan-time reduction methods that allow to reconstruct an image only from small fraction of k-space data ("compressed sensing").

The sequences have been tested for image quality, accuracy of T_2 measurements and the measurement time. The primary use of these sequences is supposed to be experiments on petroleum reservoir core plugs, where using frequency encode techniques may be problematic either due to local gradient distortions or too short T_2. They are applicable, however, to all processes accomplished by changing site-specific T_2 (cement paste hydration, curing of rubbers, filtering paramagnetic impurities, etc.)

[1] O. V. Petrov, B. J. Balcom »Measuring spatially-resolved T_2 distributions in purely phase encode MRI applications«, 10th International Conference on Magnetic Resonance Microscopy, West Yellowstone, Montana, USA (2009)

P91 **Cardinal Series as a Versatile Tool to Process NMR Signals of Porous Materials**

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The NMR spectra of porous materials are characterised by broad spectral lines, often due to intrinsic inhomogeneity of their magnetic susceptibility. Another recurrent feature of the spectra is them being a band-limited function. Herein we show that time-domain signals of those systems can be modelled precisely and effectively by finite cardinal series. Such modelling can, in turn, be used for restoration of signals should they be damaged or for design of a digital low-pass filter, which stay applicable even when experimentally acquired signals

are truncated.

[1] J. Magn Reson. 202 (2010) 147-154 D. Bytchenkoff, Stephane Rodts, Pascal Moucheront and Teddy Fen-Chong

[2] J. Magn. Reson. 204 (2010) 64-75 Stephane Rodts, D. Bytchenkoff and Teddy Fen-Chong

P92 High Frequency Modulated Gradient Spin Echo Diffusion Measurements with Chemical Shift Resolution

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In the Modulated Gradient Spin Echo (MGSE) technique [1], the diffusion dependent signal attenuation is accumulated over several rapidly oscillating cycles of modulated gradients, making the measurement sensitive to shorter time scales compared to the Pulsed Gradient Spin Echo (PGSE) experiment [2]. The motion is described in the form of a diffusion spectrum [1]. We present an MGSE pulse sequence that enables diffusion measurements with chemical shift resolution in the obtained spectra at higher modulation frequencies than previously obtained [3]. The modulation is generated using CPMG in a constant gradient [2]. To avoid distortions from eddy currents, a longitudinal eddy current delay was added between gradient modulation and spectrum acquisition. To avoid effects from gradient-slicing and unwanted coherences, we kept the sample short [2]. To maintain high chemical shift resolution using a short sample, we used a 5 mm Shigemi tube.

The experiments were performed at 25 °C on a Bruker Avance 500 MHz instrument, equipped with a commercial probe (DIFF30). The pulse sequence was tested on a sample of distilled water and a sample of a water-continuous microemulsion. (Winsor's type I) [4] (H_2O/NaCl, heptane, sodium dodecyl benzene sulfonate, 2-butanol).

The diffusion measurements in the sample of distilled water are stable up to a modulation frequency of 1600 Hz. The average diffusion coefficient obtained in the range 400–1600 Hz was 2.29×10^{-9} m^2/s, which is in very good agreement with the literature value at 25 °C [5].

No severe phase distortions were observed in the spectra of the microemulsion for modulation frequencies up to 1600 Hz. The corresponding diffusion spectrum is flat for both oil and water. The average diffusion coefficientobtained in the range 600–1600 Hz was 1.6×10^{-9} and 8.0×10^{-10} m^2/s, respectively for water and oil (heptane). The respective values obtained in a PGSE measurement with a diffusion time of 10 ms were 1.6×10^{-9} and 5.0×10^{-10} m^2/s. The water molecules are diffusing in a continuous phase between closely packed and small oil droplets (10–100 nm), so already at a modulation period of 0.6 ms the tortuosity limit is reached. Oil molecules are confined inside the small droplets, where the long-time behavior is reached already for the highest modulation frequencies.

The instability for modulation frequencies higher than 1600 Hz is due to remaining eddy currents. This may be improved by using smoother edges of the gradient pulse, or by combining a longitudinal eddy current delay with sine-shaped gradient pulses and CPMG [3].

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P93 Bipolar double-PFG NMR Reveals Pore Morphology in Randomly Oriented Cylindrical Compartments and in Spherical Yeast Cells

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Diffusion NMR is the most important methodology for non-invasively characterizing pore morphology. Scenarios such as diffusion in spheres or in locally anisotropic but randomly oriented compartments are extremely difficult to characterize using conventional single-PFG (s-PFG) MR. The angular double-PFG [1] (d-PFG) methodology at long mixing times (t_m) offers a novel means to overcome this limitation, since it provides quantitatively different angular dependencies for spheres and randomly oriented cylinders [2]: a flat angular dependence is expected for spheres, while a modulated bell-shaped function is expected for locally anisotropic but randomly oriented pores [2]. Another advantage of angular d-PFG is that it can be conducted at low q-values [3]. Here, we used controlled randomly oriented cylindrical pores, in which the inner diameter (ID) and compartment shape are known a-priori. S-PFG and long t_m angular d-PFG experiments were performed. Scanning electron microscope images confirmed that the specimen is indeed comprised of completely randomly oriented cylindrical microtubes. The line width of the water resonance in these pores was ~ 0.5 kHz, a manifestation of large susceptibility artifacts. Conventional s-PFG experiments surprisingly showed direction-dependant signal decay, clearly unexpected for randomly oriented compartments. However, when we employed bipolar gradients in the s-PFG sequence (bp-s-PFG), an isotropic decay was observed, as expected. The angular d-PFG experiments yielded inverted angular dependencies, from which microstructural information could not be obtained; therefore, we implemented a d-PFG NMR sequence with bipolar gradients (bp-d-PFG). The angular bp-d-PFG NMR yielded the expected [2] modulated bell-shaped function, providing insights that could not be inferred from s-PFG methodologies. First, the presence of restricted diffusion was easily inferred, since the non-flat angular dependencies are only observed when restricted diffusion occurs. Second, we could infer on the eccentricity of the pores, a fact we could not infer from s-PFG experiments. To demon-

strate that spherical pores yield a flat angular dependence in long t_m angular d-PFG experiments, we used a suspension of fixed spherical yeast cells. Indeed, a flat angular dependence was observed, unequivocally characterizing the pores as spherical. Very accurate pore size measurements were also obtained using these approaches for both specimens. The bp-d-PFG methodology offers a new quantitative means for characterizing pore morphology, including pore size and shape. Applying bipolar gradients clearly eliminates the significant susceptibility artifact. Therefore, bp-d-PFG NMR may emerge as the method of choice for non-invasive characterization of heterogeneous specimens characterized by compartment shape anisotropy.

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P94 NMR Relaxometry: Spin Lattice Relaxation Times in the Laboratory Frame versus Spin Lattice Relaxation Times in the Rotating Frame

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Relaxometry dispersion curves display the spin lattice relaxation rate as a function of the measurement frequency. However, as far as proton NMR is considered, dispersion curves usually start around 5 kHz and thus miss the very low frequency region. This gap can be filled by the measurement of the spin-lattice relaxation rate in the rotating frame. The issue of connecting both relaxation rates is considered for two relaxation mechanisms: i) randomly varying magnetic fields, ii) dipolar interaction within a system of two equivalent spins. Appropriate data processing is presented and the random field mechanism turns out to be adequate. Moreover, this procedure has proved to be essential for the analysis of proton dispersion curves obtained for water embedded in mesoporous media.

5.7 Porous Media in Medicine

P95 **High field MR Microimaging Investigation Gives More Insights on Spongy Bone Characteristics**

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Spongy bone (SB) is a porous system characterized by a solid trabecular network, in which pores are filled by bone-marrow. Bone-marrow is in turn constituted by water and fats at certain relative percentages, which can change under pathological conditions. The main interest in SB investigations is due to identifying parameters and procedures with the potential ability to reflect the SB status, thus prompting new perspective for osteoporosis diagnosis.

Aim of this study was to characterize, by a multi-parametric MR-microimaging approach, SB as a function of its water quantity and trabecular bone density, in order to indicate the most sensitive parameters to detect SB quality.

Using an 9.4 T system, equipped with a micro-imaging probe with a maximum gradient strength of 1200 mT/m, we investigated SB specimens obtained from calf femur heads. T_2, T_2^*, ADC and G_i (the internal gradient) parameters were measured in both spectroscopic and spatially resolved (in plain image resolution 40 μm, slice-thickness 200 μm) modalities for both components, water and fat. Relative percentages of water and fats were indirectly quantified from spectra.

Six ex-vivo SB samples, were cut into pieces of about 20 mm height and 7 mm dept, in order to fit into the micro-imaging probe bore. The longest axis of each sample was located parallel to the main direction of the static magnetic field (i.e. z direction). Samples temperature was fixed to 291 K. Gradient-Echo images were obtained to evaluate T_2^*, using GEFI imaging sequence (TR=1000 ms, NS=16) at various TEs(3, 3.2, 3.4, 4, 5, 6, 8, 10, 12, 14, 16, 18, 20, 24, 30, 40, 50, 60, 70, 80, 100, 120 ms). A MSME imaging sequence (TR=2000 ms, NS=8) at various TEs (3.2, 3.8, 4.2, 4.8, 6, 8, 10, 12, 14, 16, 18, 20, 24, 30, 40, 50, 60, 70, 80, 100, 120 ms), was also used to assess SE decay. Both T_2 and G_i were derived from the attenuation of SE signal at different TEs. A PGSTE imaging sequence was employed (TE/TR=21.9/3000 ms, $D = 80$ ms, $d = 4$ ms, using eight b-values ranging from 200 to 80 000 s/mm^2, NS=16) to measure the ADC along x direction. The analogous spectroscopic version of these spatially resolved sequences were also acquired.

We investigated the behaviour of all considered MR parameters as a function of: 1) trabecular bone density, 2) relative fat and water bone marrow concentrations, 3) magnetic susceptibility differences between water, fat and bone 4) different locations (i.e., central, close to the boundary, or in between these two) inside each pore.

We demonstrate that: a) water concentration is higher close to pore surfaces, and decreases progressively moving towards the centre of pores; b) all MR parameters measured from water (but not from fat) component, reflect trabecular

bone densities (in particular water G_i is directly proportional to trabecular bone density). We conclude that T_2, T_2^*, ADC, and, more remarkably, G_i extracted from bone marrow water component represent reliable markers to evaluate SB density and quality.

P96 High Field MR Evaluation of Internal Gradients in Porous Systems: SE versus DDIF Method

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When magnetic susceptibility differences exist between a porous matrix and a saturating fluid, local magnetic field gradients (internal gradients, G_i) develop at the interface. Recently, two different methods were used to quantify G_i in trabecular bone structures: the Spin-Echo (SE) method and the Diffusion Decay Internal Field (DDIF) method. G_i can be extracted by a fitting procedure from SE decay and ADC measurements. It can be also extracted from DDIF rate using corrections due to T_1, gradient slice rate 1/Ts and ADC values.

Aim of this study was to compare, SE and DDIF methods in evaluating internal gradients from water in packed beads and in ancient bone specimens as a function of their mean porous diameters and bone density.

Using an MR system operating at 9.4 T and equipped with a micro-imaging probe with a maximum gradient strength of 1200 mT/m, we investigated: 1) five different packed polystyrene beads samples characterized by beads mean diameter of 4, 10, 40, 80 and 140 μm, 2) archeological bone specimens obtained from different locations of human tibiae coming from an archeological site, sited near Urbino (Italy). Bone samples (cut into pieces of about 1.5 mm height and 8 mm dept) were obtained from healthy and periostitic cortical bone and from different trabecular bone zones.

T_1, T_2, ADC parameters were measured and SE and DDIF decays were collected to extract G_i from both SE and DDIF method. MSME (Multi Slice Multi Echo) imaging sequences at various TEs and at various TRs were used to assess SE decay, T_2 and T_1 from selected slices (slice thickness = 250 μm). PGSTE imaging sequences at different big delta values (with diffusion gradient strength equal to zero) and at different gradient strengths, were also used to obtain DDIF decay and ADC values respectively.

As expected, we found that G_i magnitude increases according to bone pores and inter beads dimensions decreasing. Moreover we demonstrate that: a) SE and DDIF methods applied to the same sample give rise comparable G_i values. Specifically, G_i values extracted from SE decay method showed higher values than those obtained using DDIF values b) The difference between G_i extracted from SE and DDIF methods depends on pores dimensions.

P97 **In Vivo Measurement of Membrane Permeability and Fiber Size in Calf Muscle Using Time-Dependent DWI**

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The diffusivity measured in tissue in vivo depends on the diffusion time and is sensitive to tissue microstructure. Novikov et al. [1] recently showed that the presence of randomly oriented permeable flat membranes results in a time-dependent diffusion coefficient $D(t)$, from which the values for the free diffusion coefficient, membrane permeability and surface-to-volume ratio can be estimated. Here we measure in vivo the membrane permeability and fiber size in the human calf muscle using time-dependent diffusion.

Imaging was performed on the right calf muscle of a healthy 28-year male volunteer using a 3T Siemens Trio system with a knee coil. DWI images were acquired along 6 gradients directions for $b = 100, 500 \, \text{s/mm}^2$. The DWI signal was measured at 8 different time points varying between 21 ms and 1515 ms using a standard Stejskal-Tanner diffusion weighting (TE = 42 ms), a twice refocused spin echo (TRSE) sequence (TE = 57 ms), and a stimulated echo sequence (TE = 29 ms) with mixing times increasing from 35 ms up to 1500 ms. Other acquisition parameters were: TR = 6 s, matrix = 64×64, FOV = $190 \times 190 \, \text{mm}^2$, 5 slices, slice thickness = 10 mm. DTI parametric maps were calculated using Matlab.

All major muscle groups (anterior tibialis, gastrocnemius lateralis, soleus, etc.) were considered for analysis. For all muscle groups, the largest eigenvalue in the direction parallel to fibers remains almost constant, whereas the values for the 2nd and 3rd eigenvalue markedly decrease with time. This time-dependence in each muscle group agrees well with the theory [1]. After fitting, the derived mean values (and standard deviation) over the different groups were: free diffusivity $D_0 = 1.81 \, (0.09) \, \mu\text{m}^2/\text{ms}$, cell permeability $P = 0.033 \, (0.013) \, \mu\text{m/ms}$, surface-to-volume ratio $S/V = 0.085 \, (0.026) \, /\mu\text{m}$, and cell size $a = 52.86 \, (23.52) \, \mu\text{m}$. The fitted values of cell diameters fall within the range of human muscle fiber diameters (40–120 μm) [2] and the variations between the muscle groups are consistent with published histological parameters. Values for the membrane permeability are found to be within the expected range for the cell plasma membranes in eukaryotic cells, e.g. a permeability value of 0.013 mm/ms was found in the sarcolemma of male rat calf skeletal muscle cells [3].

To conclude, our model [1] is shown to yield realistic parameters for human calf muscle fibers, consistent with our assumption that the predominant restrictions to molecular motion are cell membranes. The model provides a novel in vivo method of quantifying cell size and membrane permeability from time-dependent diffusion measurements.

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$\boxed{\text{P98}}$ **Water Diffusion q-space Imaging as a Probe of Cell Local Viscosity and Anomalous Diffusion in Grey and White Matter**

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In living tissue water do not show Eisteinian diffusion, that is, the diffusion propagator is an unknown function, not gaussian. We verify that Stokes-Einstein laws could be applicable for free water itself in an aqueous solution, and show that the root mean squared displacement (RMSD) calculated are compatible with those measured in brain. Anomalous Diffusion Imaging (ADI), Diffusional Kurtosis Imaging (DKI), Bi-exponential Diffusion Imaging (BEDI), q-space imaging (qSI) are models that allow to estimate the non-gaussian mean squared displacement of water in tissue. All these models show that the RMSD of water for diffusion times used are equal or inferior to the mean size of the cells of the nervous system, and strongly suggest that the water diffusion is sensitive to the intracellular substructures because of this small diffusion length scale. Recent progress in the view of cytoplasm as a porous media conclude that water and small solutes diffusion could be both slowed by the local microviscosity of the crowded aqueous phase, probe collision with the cytoskeleton network (with elimination of possible diffusion pathlenght by the volume occupied by the network phase), and water hydrodynamic interaction with dissolved macromolecules and with the microtrabecular lattice. These interactions have been show to determinate the phenomenological "anomalous diffusion" of probes in the cytoplasm. Arguments that microtubules structural changes could alters the diffusion decay signal in brain White Matter value are checked. Simulations shows that in q-space, the RMSD is a value dependant of a gaussian approximation, whereas the probability of zero-displacement is independent of modelling.

$\boxed{\text{P99}}$ **Water Diffusion Decay Imaging in Ischemic Human Stroke: Implication of the Role of Cytoskeletal Elements in Water Anomalous Diffusion**

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Water diffusion in biological tissue has an important characteristic to deviate from Einstein laws, and the extraction of quantitative indices of the measured noisy diffusion MRI signal (S/S_0) is an ill-posed inverse problem estimated by numerous fit models. The length scale probed by water diffusion in tissue is the same than the neurons, astrocytes, dendritic radius size. Then, we investi-

gated the interdependence between the length scale of this network and water as an endogenous probe of the intracellular cytoskeletal structure. Arguments that slowed water diffusion in tissue and water diffusion changes in energetic failure is probably caused by the cytoskeletal network are examined. Based on modern biological and biophysical experimental view of the cytoplasm as a fractal porous media, we derived a conceptual model of water diffusion in the crowded cytoplasm. Modeling of the MR Diffusion Decay Imaging (DDI) and Inverse Laplace Transforms (ILT) of the decays were used to investigate the quantitative change of water diffusion in human sub-acute ischemic event, that could light the cause of the non-Einsteinian behavior of water diffusion in living tissue. Simulations of ILT of the decay shows that ILT is able to discriminate anomalous diffusion of one pool of water (as observed in grey matter) versus two pool of water with gaussian diffusion or kurtosis deviation (as in white matter). Ischemia cause a shift of a single distributed pool of grey matter water to two pools, whereas in ischemic white matter the two pools (or kurtosis deviation of one pool) change only by their intensity.

P100 Weakly Restricted Diffusion Studies Using Polarized ^{3}He at Ultra-Low Magnetic Field

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Lung magnetic resonance imaging (MRI) using polarized ^{3}He gas provides information about flow in the airways, ventilation properties, lung function (by O_2 concentration measurements) and lung microstructure (by diffusion measurements). The system of airways in human lungs has a fractal structure and starts with bronchial tubes (diam. $\sim 2\,\mathrm{cm}$) and ends with hundreds millions of alveoli (diam. $\sim 0.15\,\mathrm{mm}$). Depending on imaging conditions (gradients, timings), diffusion of ^{3}He gas in those airways can vary between free diffusion, motional averaging or localization regimes. We will present studies of the impact of diffusion on NMR signal attenuation in crossover diffusion regimes where no reliable theory exists for the interpretation of data obtained in clinical research.

Most of the studies of lung MRI using ^{3}He gas have been made at 1.5–3 T magnetic fields on standard commercial systems. The use of the polarized gas allows for high and nearly field-independent signal to noise ratio (SNR) over a broad range of field values. There are several advantages of using low magnetic fields: very long precession times (T_2^*) for NMR signals, negligible rf-heating of tissues, low cost of equipment, etc [1-3]. To explore the potential of such ultra-low fields, we have build a compact 1:4-scale model of a whole-body imaging system (it includes a resistive magnet, imaging gradient coils, and NMR coils). This system operates at $\sim 2.7\,\mathrm{mT}$ magnetic field / $85\,\mathrm{kHz}$ frequency. Combining the high detection bandwidth ($\sim 10\,\mathrm{kHz}$) requested for imaging and low thermal noise (i.e., high Q-factors) is challenging at this frequency, but was obtained using appropriate detection schemes.

Several sealed [3]He cells have been used as samples: $5\,cm \times 5\,cm$ ($67\,mbar$) and $12\,cm \times 1.8\,cm$ ($400\,mbar$). Nuclear polarization of [3]He gas was $\sim 5\,\%$, obtained in situ by laser optical pumping. Multiple spin-echos were obtained by CPMG and PGSE techniques. Their attenuation rates were studied over a wide range of timings and applied gradients. The same crossover regime as occurs in lung airways up to acinar level (weakly restricted diffusion) has been explored in this experiments.

We also perform [3]He imaging of plastinized small animal lungs in our system and current work will be reported.

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5.8 Porous Media in Environmental Science

P101 Detection of Karst Caverns and Estimation of their Volume Using Magnetic Resonance Soundings

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For better understanding of the Dead Sea sinkhole phenomenon we applied the Magnetic Resonance Sounding (MRS) method to investigation of potentially dangerous sites.

MRS signal is measured using a wire loop on the surface that is applied as transmitting and receiving coil. After inversion, MRS provides estimate of the water content and of the relaxation time T_1 as a function of depth. MRS water content is linked to the volume of groundwater within investigated area and the relaxation time depends on the mean size of water-saturated pores. MRS results are averaged over investigated volume that depends on the loop size. For our study we used a $100 \times 100\,m^2$ square loops.

When investigating karst aquifers MRS signal generated by bulk water in the caverns is characterized by a long relaxations time what allows reliable identification of the caverns. In porous media MRS estimate of the water content required additional calibration, but an average volume of bulk water in the caverns may be estimated without calibration.

The investigated area is located on the central part of the Dead Sea shore of Israel. The subsurface is composed of alluvial-fan sediments down to a depth of about $20\,m$, a several meters thick marl layer, a salt layer (about $10\,m$ thick), and intercalated clay and gravel layers below the salt. Groundwater water has a total salinity of about $340\,g/l$ and an electrical resistivity of about $0.05\,\Omega m$.

In rocks, a resistivity between 1 and $0.6\,\Omega$m (locally near $0.25\,\Omega$m) is typical for the area.

Fourteen soundings were performed with a $100 \times 100\,\text{m}^2$ square loop through the area of $300 \times 400\,\text{m}$ comprising both sinkholes and intact area. The low level of electromagnetic interference observed during the fieldwork allowed us to measure even small signals. The amplitude of the MRS signal varied between 10 and $100\,\text{nV}$. All MRS measurements were done with the NUMISplus MRS system (IRIS Instruments, France). Each MRS measurement was accompanied by Transient EM (TEM) measurements with the TEM FAST 48 HPC system (AEMR, The Netherlands).

Penetration depth of the MRS signal was estimated as 30–40 m. Relaxation time T_1 varied in the range of 50 to $1000\,\text{ms}$. Short values of T_1 (50–$150\,\text{ms}$) were interpreted as silt and clayey soils, whereas long values of the relaxation time T_1 ($>500\,\text{ms}$) are an unambiguous signature of bulk water in the subsurface. Considering the geology, the aquifer detected by MRS was interpreted as a karst aquifer. The karst zone was located and the volume of karst in the investigated area was estimated with MRS as $27,000 \pm 13,500\,\text{m}^3$, corresponding to 3.5 to $10\,\%$ of the salt formation volume.

P102 Water Flow from Soil to Roots Investigated by MRI

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Water flow in soils is one of the most important functions that control the water supply for root and plant growth. Since flow velocities in soils are mostly too slow to be monitored directly by MRI flow velocity imaging, we used Gd-DTPA as tracer for the first time to visualize flow processes in soils [1]. Apart from its chemical stability it turns out that the main advantage is the anionic net charge in neutral aqueous solution which hinders the adsorption at soil mineral surfaces and therefore avoids retardation. To obtain optimal measurement parameters the relation between signal intensities, tracer concentrations, repetition time t_R und echo time t_E were investigated in a preliminary study. The images were measured with a spin echo multi-slice sequence with strong T_1-weighting (e.g.: $t_R = 0.2\,\text{s}$, $t_E = 2.7\,\text{ms}$, $0.16 \times 0.16 \times 0.9\,\text{mm}^3$ voxels).

Water flow has been investigated during i) infiltration and ii) injection experiments of unsaturated model soils with maize and lupin plants. During the infiltration experiment we observed initial rapid homogeneous wetting of the bulk soil from the bottom, whereas the immediate vicinity of the root is not reached by the tracer. After this initial period a continuous enrichment of the tracer is observed in this region within the next hour, but no uptake by the plant. Furthermore, injection experiments were performed to decouple the wetting from the transport process.

Under bright illumination different steps could be observed: Dispersive spread-

ing of the plume in the soil, followed by directed flow to the root system, enrichment in the cortex of the roots, and final transport upwards in the xylem. Under dark conditions spreading of the plume is still present, but Gd-DTPA is now taken up so slowly that it is not enriched in the cortex but actively transported with the water to the xylem. With these results active and passive uptake of Gd-DTPA can be distinguished and conclusions on the water flux processes can be drawn. The soil structure determining the flow process was additionally investigated by relaxometric imaging ($t_E = 4\,\mathrm{ms}$, $n_E = 64$, $0.32 \times 0.32 \times 0.6\,\mathrm{mm}^3$ voxels).

These first results show that the root-soil interface possesses a small zone of higher water content und homogenous relaxation times around lateral roots corresponding to the extension of the root hair zone and may serve as water buffer for roots.

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P103 Electrokinetic Desalination of Porous Building Materials: an NMR Study

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The deterioration of porous building materials and structures by the crystallization of water soluble salts is a well known phenomenon. The removal of salt from the zone of deterioration is one of the possible solutions to minimize the threats posed by salts to porous materials. To desalinate the building materials electrokinetic method has been used. In order to obtain non destructive measurements of both the moisture and salt ions (Na+ ions) transport through porous building materials during the desalination treatment an NMR setup has been used. In this study the effect of the applied electric field on the migration of salt ions through fired clay bricks is examined by varying the field gradient from $0.75\,\mathrm{Vcm^{-1}}$ to $2\,\mathrm{Vcm^{-1}}$ across the specimen. The contribution of diffusion on the transport of salt ions is also studied by introducing a concentration gradient across the brick. The measurements show that to exceed ion diffusion a minimum level of applied voltage is necessary. Below this threshold voltage, diffusion is dominant over electromigration. The effect of advection on the salt transport is also studied by introducing a hydraulic gradient across the specimen. The results show that advection is a major transport mechanism in the materials studied. Furthermore, the transport of salt ions can be enhanced if both the hydraulic and potential gradients are applied in the same direction, but if applied in opposing directions the desalination process is halted.

P104 Incorporating Internal Gradient and Restricted Diffusion Effects in NMR log Interpretation

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It is well known that in the NMR study of fluids in a porous media, the internal gradient may distort the signal significantly. The internal gradient is proportional to the strength of the external magnetic field and the susceptibility difference between the matrix material and the pore fluids. In the case of sedimentary rocks that contain magnetic minerals, even low magnetic field can generate strong internal gradients that obscure the gradient from the external field and result in inaccurate fluid typing in the D–T_2 cross plot. The problem of the internal gradient is further complicated by the restricted diffusion effect, as pores of different sizes pose varying degree of restriction within the time scale of NMR measurements. To date, studies on these effects focus on either the experimental characterization of the internal gradient, or the relaxation behavior under ideal models. Due to the complexity of the pore system and the unknown distribution of magnetic materials in the rock matrix, a practical solution that incorporates restricted diffusion and internal gradient effects in the D–T_2 log interpretation has never been proposed.

In this paper we propose a possible solution to this problem. First we model restricted diffusion in the presence of the internal gradient to produce synthetic data and to demonstrate that the synthetic data can be interpreted inaccurately with conventional assumptions. The synthetic data is generated by numerically solving the Bloch-Torrey equation, assuming a certain pore shape and internal gradient distribution. Secondly we devise a new 2D inversion processing scheme based upon the new model that includes internal gradient and restricted diffusion. The new scheme takes advantage of the discrete nature of the inversion and pre-generates a large set of matrixes to be used in the inversion. The scheme is shown to work on the synthetic data, and proven applicable to real well log data. Thirdly, a comparison between the log processing results from the conventional method and those from the new method demonstrates that the new method yields more accurate fluid typing and quantification results. The new method is particularly useful for low-pressure or depleted gas wells where the weak gas signal is ambiguous to start with. It makes the interpretation of 2D maps more robust as the fluids are now displayed on 2D maps closer to their theoretical expectations. By explicitly including the internal field gradient and restricted diffusion effects, the proposed method increases the likelihood that other formation characteristics, such as wettability-caused T_2 shifts, can be discerned from these effects.

$\boxed{\textbf{P105}}$ **Analysis of Spectral Influence of the NMR CWFP Parameters in Flow Quantitative Measurements**

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The NMR-CWFP pulse sequence (Nuclear Magnetic Resonance - Continuous Wave Free Precession) has met several applications in the science. The present work analyses the high sensibility of this sequence to its spectral parameters variation, exclusively in a theoretical and experimental characterization of the flow NMR-CWFP of the kind plug-flow, exemplified by online measures by seeds transport through a mat under a magnetic field constant in time, with a small gradient.

Simulations and measurements were made on several conditions, varying the factors that have measurement influence, like flip angle, offset angle, time between pulses (T_p), gradient (G), velocity (v) and longitudinal and transversal relaxation times (T_1 and T_2). In a first hand, the theoretical results were made through a Bloch matrix approach, in an iterative algorithm, in each pulse interval. On the other hand, the experimental data were collected with a CAT 100 Tecmag Apollo hardware, in a Oxford $2.1\,T$ magnet, with a offset phase of $5\,MHz$. In general, the samples were oil seeds, like linseeds, soybean and castor bean, exampling different T_1/T_2 rates. For driving the mat, a new software NMR Automation was done in a Visual Basic language, where space, velocity and acceleration could be controlled.

Under certain conditions of flip angle, precession, time between pulses, gradient and velocity, it was noticed that there might be a null point with T_1 and T_2 dependence. For example, in a low rate T_1/T_2, the null point was in a really low velocity, when for high rate T_1/T_2, high velocity is needed, and the signal showed constant for low velocity. Experimentally, just low velocity could be measured, but still could be seen influence of the velocity in the amplitude of the CWFP signal. The null point phenomenon was studied and a new selective method through relaxation times was suggested. The work validated also the CWFP pulse sequence as a quantitative tool to quantitative analysis of seeds oil mass, with a potential for more than thousand seeds in an hour interval. We thank the Brazilian researcher agencies CNPq and FAPESP.

$\boxed{\textbf{P106}}$ **Slow Flow in Natural Porous Media Monitored by MRI**

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Besides the gas phase, water is the universal transport medium for nutrients and contaminants in soils. The corresponding flow processes are characterised by slow flow velocities and sensitivity for external disturbances. Therefore MRI in combination with tracer is very convenient for non-invasive monitoring. Necessary is a tracer which behaves conservatively, e.g. it should not interact with

the solid matrix and a good contrast should be achievable. For these reasons we have chosen the chemically stable complex Gd-DTPA containing the strong paramagnetic Gd^{3+} ion. In a preliminary study the relation between signal intensity, tracer concentration, repetition time t_R und echo time t_E was investigated. For the following experiments we applied a spin echo multi slice sequence with strong T_1-weighting (e.g.: $t_R = 0.2\,s$, $t_E = 4.8\,ms$, $1.3 \times 1.3 \times 2\,mm^3$ voxels).

Measurements on the flow of Gd-DTPA in natural porous media were performed under two different boundary conditions: Gravitationally and evaporation driven flow. In the first case a model column consisting of an inner highly conducting core of medium sand surrounding by a less conductive out core of silt was irrigated from top under steady state conditions. In doing so the tracer plume moved homogenously only through the inner core. This behaviour was validated by soil physical simulations based on the basic parameters: structure, density, water characteristic, and hydraulic conductivity. The second set-up for gravitational flow was a natural soil column of a sandy loam also irrigated under steady state conditions. The short relaxation in this system required the further reduction of $t_R = 0.05\,s$ and $t_E = 1.9\,ms$. In contrast to the model column the flow behaviour is more complicated. First of all the plume moved along defined pathways. Local flow velocities are higher than the average flow velocity which is characteristic for preferential flow phenomena. The third set-up is a continuation of the first one, i. e. the infiltration of the tracer plume is stopped after a certain distance and the following upward flow, which is now driven by evaporation from the surface, is monitored. The previous assumptions about internal redistribution of tracer near the surface and deeper in the porous system, as implemented in previous soil physical simulation, are validated by MRI, which allows a non-invasive look inside the »black box«.

P107 Metastable Sodium Sulfate Heptahydrate, as Studied by NMR

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Salt weathering is a major cause of deterioration of our cultural heritage. Of the salts responsible, especially sodium sulfate is seen as very damaging. Sodium sulfate can have three main crystalline phases: thenardite (Na_2SO_4, anhydrous salt), mirabilite ($Na_2SO_4.10H_2O$) and the thermodynamically metastable heptahydrate ($Na_2SO_4.7H_2O$). However, many questions have emerged in recent years concerning which crystalline phase is formed during salt weathering and hence what the real damaging mechanism is.

In this study we combined NMR for measuring non-destructively the moisture and sodium content with a digital microscope for imaging analysis. This combining gives the possibility to directly relate the measured concentration with the crystal being observed, and also with the crystal growth speed. In these experiments the crystallization was induced either by cooling down the sample or by drying.

Experiments were performed with a droplet on both wetting and non-wetting surfaces. In almost all experiments, i.e. in 95 % of cases we observe the formation of heptahydrate, the metastable phase of sodium sulfate. The crystallization of heptahydrate has been also checked by DSC measurements. Hence, the nucleation of heptahydrate is relevant for understanding of crystallization and damaging mechanisms of sodium sulfate in porous media.

P108 NMR Soil-Moisture Sensor for Field Measurements

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We present a prototype of a moisture sensor that can be deployed in the field to measure the NMR signal of water in bore holes. It consists of a cylindrical magnet core, magnetized perperdicular to its main axis and a planar radiofrequency (rf) coil in the center of the magnet. A simple impedance matching circuit is enclosed in a metallic box at one end. The sensor has a diameter of 48 mm and a length of 260 mm.The rf coil is of the figure-8 type, which makes it less sensitive to far-field noise and reduces the acoustic ringing. With this configuration of the coil and the magnet the sensitive volume is located 9 mm away from the surface of the coil at a Larmor frequency of 9.9 MHz. Water signals in soil are measured with a CPMG pulse sequence using an echo time of 60 μs. Upon calibration, the data so obtained can be directly transformed to partial water saturation of the soil. Field measurement done at the Selhausen site demonstrated the capability of the sensor to follow the evolution of moisture due to evaporation and precipitaton. Furthermore, data at good enough signal-to-noise ratio were analyzed with an Inverse Discrete Laplace Transformation (ILDT) to obtain relaxation spectra that gives information about the microscopic environment of the water retained in the soil. One first result is the observation of relaxation enhanced by the influence the surface of the solid matrix upon decreasing saturation, a result already found by another group recently [1]. Further developments of this instrument can lead to a new tool for in situ studies of soil not only to measure moisture but to take advantage of all the information NMR can provide about soil as a porous medium.

[1] Stangaciu, L. et at. WATER RESOURCES RESEARCH, VOL. 45, W08412, doi:10.1029/2008WR007459, 2009

5.9 Porous Media in Renewable Resources and Food Science

P109 **Assessment of the Specific Surface Area of Fat Crystal Networks by Diffusion NMR**

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The Specific Surface Area (SSA) is widely used to predict and control physical properties of structuring agents in product formulations. Different measurement methods are in use, but the application scope varies with matrix and underlying physical models used for interpretation of the data.

Two different model systems having a coarse and fine fat crystal network were made by dispersion of solid fat in water and oil respectively using different shear forces. D-NMR was used to assess the surface-to-volume ratio of the fat crystal network for short diffusion times from which the SSA was calculated. The latter was compared with indicative values obtained with XRD analysis for the fine fat crystal network model system dispersed in oil. The ratio solid fat versus liquid phase for the model systems were chosen such that both short and long diffusion time behaviour effects were observed within the diffusion range of the D-NMR experiments.

Results for the fine fat crystal network dispersed in oil showed that the calculated self diffusion coefficient of oil for short diffusion times did not match with the theoretical value. The obvious reason is non-elastic collision between the liquid oil and the solid fat surface. It is assumed that this does not influence the calculated SSA, which was comparable with XRD analysis results. For the coarse fat crystal network dispersed in water results showed that the calculated self diffusion coefficient of water did compare with the theoretical value, meaning elastic collision between the water and the solid fat surface. The calculated SSA was lower than for the oil continuous fine fat crystal network due to the lower applied shear force and confirmed by SEM.

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