POSTERS

Nuclear magnetic relaxation and diffusion of gas in partially water saturated natural soil

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Nuclear magnetic resonance (NMR) of fluids has proven to be a very sensitive tool for the characterization of porous systems. In general, nuclear magnetic relaxation and the restricted diffusion of water molecules obtained from water saturated porous systems can provide a wealth of information including the pore surface-area-to-volume ratio, the average pore size in systems and the visualization of fluid transport under flow. However this approach is usually limited to probing length scales ~20 μm, because spin relaxation quenches the NMR signal before molecules can diffuse across longer distances. For this reason, liquid phase NMR has been unable to give information about the long-range properties of porous media, e.g. interconnectivity and tortuosity of the pore space[1]. In contrast, NMR techniques based on an imbibed inert gas has some advantages, e.g., gas diffusion coefficients are typically orders of magnitude larger than those of water, and the weak interaction of inert gas molecules with pore surface leads to long NMR lifetime. In addition, the diffusion coefficients of the gases can be altered by varying pressure, which significantly expands the range of distances that can be probed in comparison to liquid NMR.

NMR spectroscopy of noble gases has been used for years to probe physical properties of porous media. Particularly ^{129}Xe NMR has become popular because of its exceptional sensitivity to local environmental effects. The inherent disadvantage of low spin density of ^{129}Xe is overcome by high-pressure set-ups and hyperpolarizing techniques[2]. Despite this, it has been observed that ^{19}F NMR of the multinuclear fluorinated gases possess great potential for transport and material studies since they are relatively inert, of high density, and have short relaxation times that can be used in fast imaging and lead to image qualities not much inferior to those obtained with liquids[3].

Here we have studied the nuclear magnetic relaxation times and the diffusion properties of the fluorinated gases (SF_6, CF_4 and C_4F_8) in dry and partially water saturated natural soils to characterise the soil pore space as well as water distribution and transport in soils, which depends on a variety of parameters. The most important ones are 1) the pore structure, i.e., the pore size distribution and pore connectivity, 2) the wetting properties, and 3) the directional water supply by unsaturated water fluxes. The spin-spin relaxation times and the diffusion coefficients of those gases are changed in presence of the soils. This indicates that the dynamics of the gas molecules are affected by the pores of soils. To get more detailed information about the pore space and the long-range connectivity of soil, spin lattice relaxation and time dependent diffusion experiments at different gas pressures have been done and the observed results are compared to known soil properties[4].

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Time-dependent diffusion coefficient of fluids in partially filled porous media

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Diffusion of water and organic solvents partially filling porous media is measured as a function of time in the stray magnetic field of a single side NMR_MOUSE device. The stimulated spin echo sequence [1] with constant magnetic field gradient (in the order of 10 T/m) is used. The liquids are confined in porous silica glasses with mean nominal pore sizes of 1 μm and 10 μm, and porosity of 43% and 36%, respectively.

In completely filled pore spaces, the transport properties are predominantly affected by the geometrical restrictions, i.e., the tortuosity. The time-dependent diffusion coefficient $D(t)$ then exhibits a reduction from the molecular diffusion coefficient D_0 in bulk when increasing the diffusion time. When the porous media are non-saturated, the effective diffusion coefficient is modified due to the presence of the vapor phase and the reduction in the volume of the liquid fraction. Exchange between liquid and its vapor phase can produce an enhancement in the diffusion process [2]. But in the general case, $D(t)$ has opposite tendencies upon reducing the filling fraction (enhancement or reduction) depending of several parameters like nature of the solvent, pore size or pore structure [3,4]. A general two-phase exchange model recently published (see Ref. [3]) accounts for these features. At the diffusion times used in those studies (200 and 300 milliseconds), fast molecular exchange between the liquid and vapor phase was observed in the case of nanometer length-scale confinement. However, the fast exchange regime is not valid anymore when the pore size is in the order of micrometers. This is evidenced in the attenuation of the stimulated echo versus the square of the wave number which is not exponential. That deviation depends on the mean residence time of molecules in the liquid phase.

In the present contribution the diffusion studies are performed in partially filled porous media for different diffusion times. The length scale of the pore diameter is extended to the order of tenths of micrometers. The molecular exchange model of reference [3] for the vapor and liquid phases is applied. It is found that the average residence time in the liquid phase at low filling factors is in the order of milliseconds for porous samples with ten micrometers pore size. The influence of spin-lattice relaxation, T_1, at long diffusion times is also discussed in particular at low filling factors.

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Poly(dimethyl siloxane) films adsorbed in porous media

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The dynamics of polymer thin (i.e. nm-scale) films is becoming of growing interest both from an experimental as well as theoretical point of view; its investigation with NMR methods is still a rather new field and usually requires the existence of a large surface area as is given in porous media. Under these circumstances, the actual spatial distribution and molecular conformation of polymers at very small amounts remains an open question; the assumption of equally thick films must break down at a particular amount of polymer that depends on the interaction parameters with the surface, but certainly below the value required for generating a complete coverage (monolayer). In the present study, this aspect is addressed by investigating the molecular dynamics of a linear flexible polymer, poly(dimethyl siloxane) (PDMS), confined at amounts corresponding to a few to less than one monolayer inside microporous alumina membranes of well-defined pore shapes using NMR techniques. Employing Fast Field Cycling (FFC) NMR provides information about motion in the kHz to MHz range of frequencies which can be compared with the established models observed for bulk[1] and completely confined polymer chains[2] while transverse relaxation and Double Quantum (DQ) NMR have been used to study slow dynamic processes and ordering.

Using FFC, is can be shown that the dynamics gradually slows down in films of all thicknesses, while there is a qualitative deviation from bulk behavior for the lowest polymer coverages, equivalent to one monolayer or less. The effect of temperature on relaxation is likewise less pronounced for decreasing polymer amounts. Transverse relaxation decays of these systems were found to be multiexponential in all cases, unlike the much simpler behaviour of the bulk melts; data are discussed in terms of Inverse Laplace Transforms of the decay curves and were compared to a simplified biexponential fit.

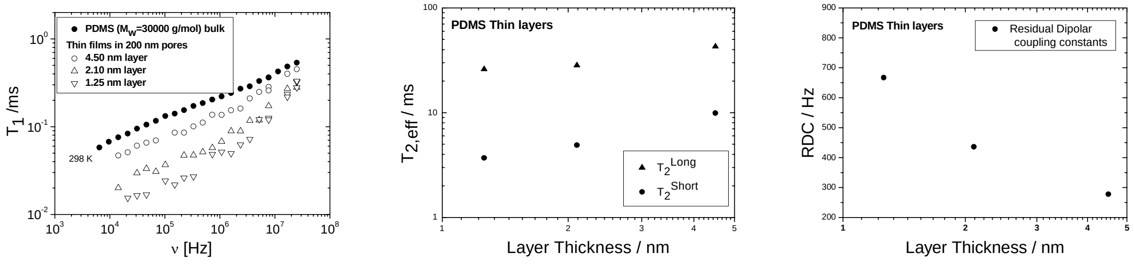

Fig. 1: Relaxation behavior of PDMS (M_w=30000 g/mol) films inside alumina pores of size 200 nm. (Left) FFC relaxation profile, (center) $T_{2,eff}$ times and (right) RDC constant of films with varying nominal thickness.

By applying DQ NMR, the existence of dynamic heterogeneities in these films is confirmed, and the values of the Residual Dipolar Coupling (RDC) constants indicate an increase of order with decreasing nominal film thickness. PDMS of different molecular weights has been studied in two different geometries and was compared to other types of polymers, allowing to draw conclusions leading to a tentative pictorial model of the actual spatial distribution of polymer molecules on internal surfaces of porous media.

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Fast Field Cycling Relaxometry: From Saturated to Unsaturated Natural Soils

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Soils as natural porous media exhibit the important ability of water retention and transport. Both properties are mainly controlled by the pore size distribution, which is furthermore related to NMR relaxation times of water molecules. In this study the longitudinal relaxation time T_1 is determined by fast field cycling relaxometry (FFC) at low fields corresponding to Larmor frequencies between 5 kHz and 20 MHz.

In this work[1] we investigated three natural soils (Sand FH31, Kaldenkirchen and Merzenhausen) which cover a broad range with respect to their texture, i.e. from fine sand to silt loam. In addition we decreased the water contents from saturation of 100% down to 6% corresponding to naturally occurring conditions.

The results of T_1- relaxation time distributions are obtained by the analysis of the T_1 relaxation curves by means of the inverse Laplace transformation[2,3]. For example Kaldenkirchen soil shows relatively broad bimodal distribution functions $D(T_1)$ in contrast to sand FH31 with an narrower unimodal behavior (Fig.1,see lower case). Using the Brownstein-Tarr model[4] for NMR relaxation in porous media we get first information about the pore size distribution which reflects the T_1 relaxation behavior scaled by the surface relaxivity. In fine sand nearly all water is present in macropores with characteristic T_1 of about 1000 ms. The opposite is found for Merzenhausen silt-loam, i.e. T_1 is about 2 ms corresponding to the major water fraction present in micropores. Kaldenkirchen with more than 10 % of silt and clay represents an intermediate case.

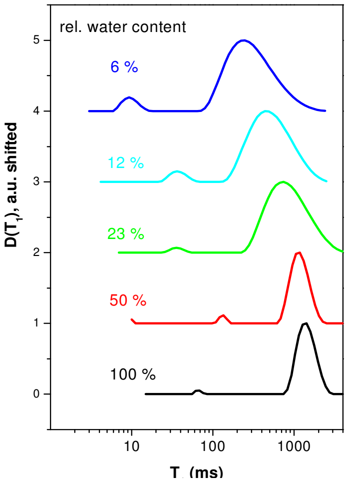

Fig. 1: T_1 distribution functions of fine sand at a Larmor frequency of 20 MHz.

With decreasing water content we observed a considerable decrease of T_1 relaxation by factors of five to ten (e.g. fine sand in Fig. 1). Independent of the exact texture of the soils a general trend is conceivable, where first macropores desiccate leading to thin water films and residual water at grain contact points (Fig. 2).

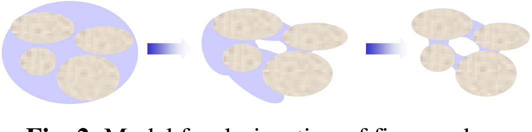

Fig. 2: Model for desiccation of fine sand.

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Low Field NMR of Water in Soils. A Case Study.

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The evolution of water in soils is a physical phenomenum of importance in soil science and climatology. While most investigations of soil moisture are performed inside large superconducting magnets in the laboratory, this eventually needs to be studied by mobile NMR equipment in the field. As a part of a DFG-funded interdisciplinary project (TR32), this work establishes preliminary results from the use of mobile NMR to measure moisture in soils. To demonstrate the ability of the NMR technique to follow the drying process of water in soils, daily moisture measurements were performed with a mobile NMR endoscope on three different types of soil (silt, sand, and a natural soil sample). The soils were packed in columns approximately 1 meter high. The NMR measurements were cross-validated by repetitive measurements of the mass drift due to the drying process. The NMR-endoscope exhibits a cylindrical geometry incorporating the principle of the u-shaped NMR-MOUSE. It could be raised and lowered inside a plastic tube in the soil column similar to a wire-line logging tool. For the purpose of modelling, a simulation of the water evolution (described by the Darcy Equation) was executed with the Hydrus1D Program for comparison with the experimental results. The optimization of the endoscope, the measurements, and the simulations are discussed as well as, the statistical uncertainty and the noise shielding.

Monitoring Water Fluxes in Porous Media by Magnetic Resonance Imaging using D_2O as a tracer

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Soil functions like water and nutrient supply for food production are strongly controlled by water fluxes in these unsaturated natural porous media. As well known, MRI is a very powerful method for non invasive monitoring of such flow processes. But for that purpose the usage of tracer substances is essential since flow velocities are relatively slow (i.e << mm/s). In the past most prominent tracers were paramagnetic ions (1,2). However, their major drawback is possible sorption at the solid-liquid interface which may cause considerably slower, apparent transport velocities than the liquid flow that is of interest. From this perspective D_2O seems to be an ideal tracer due to its high chemical similarity to H_2O.

In this study (3) we first investigated the behaviour of D_2O as tracer in an unsaturated, heterogeneous model soil composed of fine sand and a built-in cylindrical obstacle in order to force the flux around it. Water was purged in steady state through the column at a constant water potential of 39 cm (corresponding to a negative pressure of 3.8 kPa) applied at the lower boundary. Tracer pulses of 55% (w/w) D_2O and for comparison of 0.01 M $NiCl_2$ were repeatedly applied with infiltration water. The motion of the tracer plumes were monitored by MRI using a fast spin echo sequence over a period of 20 minutes with mean pore water velocities between 0.21 and 0.82 cm min^{-1}. The most important result is that the motion of the D_2O-pulse is not retarded and moves with the water flux combined with smearing by dispersion. Furthermore, the motion of the Ni^{2+} tracer as reference under known, non-adsorbing conditions (pH = 5) corresponds to that of D_2O.

In order to validate the experimental results we compared the observed motion with an independent simulation based on the Richards and van-Genuchten equations for water flux in unsaturated porous media and the convection-dispersion equation for tracer transport as implemented in the model HYDRUS2D (4). Fig. 1 compares the position of the tracer cloud 7 minutes after injection with the corresponding simulated scenario. The agreement proves that D_2O really behaves as conservative tracer and thus opens up a new field of applications.

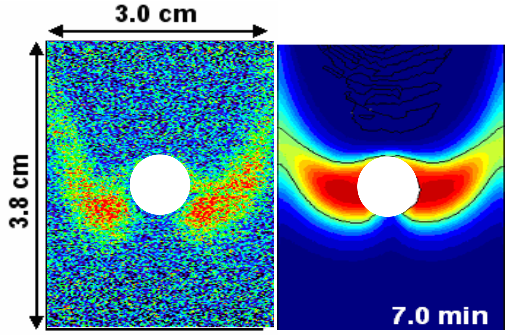

Fig. 1. Left: D_2O tracer cloud 7 minutes after injection, right: simulated tracer cloud for the same time point

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Molecular motion and glass transition for ethylene glycol adsorbed in zeolites

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Structure and mobility of molecules adsorbed in restricted geometry like zeolites has been widely investigated by means of NMR spectroscopy [1-3] by using rare nuclei (like e.g. ^{13}C and ^{15}N), where a sufficient spectral resolution could be achieved. In case of proton NMR spectroscopy, however, the applicability of NMR spectroscopy to molecules adsorbed on surfaces is often limited due to the poor resolution. A notable enhancement in resolution of the spectra may be achieved when the susceptibility broadening is averaged out by the application of MAS techniques. In all these studies the definite preparation of the MAS samples *in vacuo* plays a decisive role. It will be shown how these special measurements could successfully be realized.

Furthermore, we will discuss how the information on thermal mobility derived from the side-band analysis in ^{1}H MAS NMR experiments can be combined with the study of proton spin-lattice relaxation over a wider temperature range. The results obtained will be also compared with of broadband dielectric measurements. The results will be compared with extensive dielectric studies by Kremer et al. [4-5] on comparable systems. The main question is whether the adsorbed species show a so called single-molecule behavior characterized by an Arrhenius type temperature dependence of the respective dielectric relaxation times. In contrast, a Vogel-Fulcher-Tammann (VFT) type temperature dependence of the (mean) dielectric relaxation rate points to collective motions and is typical for the appearance of a glass-transition. We will discuss how this transition depends on the filling factor of the zeolites, on the geometry of the internal voids in our porous materials and the competition between molecule-to-molecule and molecule-to-surface-interactions. The importance of the choice of the matrix system will be shown for the case of the NaX zeolites with well-defined dimensions of the supercages. To get further insights in the complex dynamics of confined molecules, ^{2}H NMR line shape and spin-lattice relaxation measurements over a wide range of temperatures were also included.

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Studies of barium titanate embedded into mesoporous sieves and isolated barium titanate fine particles

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Phase transition temperatures, electrical polarization, coercive field, and other properties potentially depend on the particle size. In order to study size effects in barium titanate ($BaTiO_3$) it was embedded into MCM-41 mesoporous materials and the behaviour of the samples was studied in comparison to the bulk barium titanate and very fine $BaTiO_3$ powders. The MCM materials used possess effective diameters of channels of about 3.7 nm. The filling of the small pores was controlled by nitrogen adsorption isotherm measurements on empty mesoporous sieves and those filled with $BaTiO_3$. The ultrafine $BaTiO_3$ powders were prepared from a monomeric metallo-organic precursor through combined-solid state polymerization and pyrolysis (CPP method) [1]. The particle diameter varied in the range between 15 and 155 nm and the powders were carefully characterized by FT-Raman, XRD, and other methods.

Dielectric measurements were carried out for the MCM-41 molecular sieves filled with barium titanate. In contrast to the large dielectric constants (d. c.) measured for the bulk $BaTiO_3$ in the tetragonal phase, the d. c. values of the $BaTiO_3$/MCM-41 materials practically did not differ from those measured for the empty MCM-41 rods. The behavior shows that the materials do not have the ferroelectric properties. To prove this conclusion further measurements on SBA 15 samples are in progress.

The conclusion derived from the MCM-41 samples is consistent with the critical diameters estimated for very fine $BaTiO_3$ powders. The influence of the grain size on properties of the ultrafine barium titanate powders was also investigated by ^{137}Ba NMR. NMR spectra were measured for central transitions. The line shape was calculated assuming a dominant influence of the quadrupole coupling and the validity of the second order perturbation theory. These suggestions were verified by measuring the spectra at different magnetic fields (9 and 17.6 T). Temperature dependencies were measured within a large temperature interval in the ferroelectric tetragonal phase including also the 1st order phase transition from the tetragonal to the cubic phase. The complex NMR lines were deconvoluted into two lines [2] which revealed two different structures for the fine particles. The line shape parameters estimated for both of the contributions will be measured over a broad range of temperatures including the phase transition from the cubic to the tetragonal phase for the bulk material. This analysis allowed us to derive detailed conclusions about confinement effects. The results will be also analyzed in comparison to the results obtained in previous ESR measurements on nanoparticles [3].

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Mixture diffusion in porous media studied by MAS PFG NMR

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One novel combination of MAS NMR and PFG NMR techniques was applied to study the diffusion properties of molecular mixtures absorbed in nanoporous materials. MAS PFG NMR provides high resolved spectra and allows the performance of selective diffusion measurements in mixtures [1].

Diffusivity in binary mixtures of n-butane and isobutane adsorbed in zeolite MFI silicalite-1 were studied in dependence of temperature and partial concentration [2].

The diffusivity of both n-butane and isobutane absorbed in MFI differ in more than one order of magnitude. The diffusion coefficient of n-butane in mixture presents a strong dependence with the partial concentration, see Fig. 1. It was found that n-butane diffusivity decreases with increasing amount of isobutane, and presents one strong drop or discontinuity at about 0.5 n-butane molecules per channel intersection. Further on, with decreasing content of n-butane (increasing content of isobutane) the diffusivity of n-butane drops exponentially, with the value extrapolated to zero loading of n-butane coinciding with the pure isobutane diffusivity. Molecular simulations are in good agreement with these experimental results. CBMC simulations show that n-butane can locate along either straight or zig-zag channels of MFI and isobutane locates preferentially at the intersections. Molecular simulation has shown that at 0.5 isobutane molecule per intersection, the molecular traffic of n-butane is brought to a virtual stand-still because of blocking of the intersection sites by isobutane molecules.

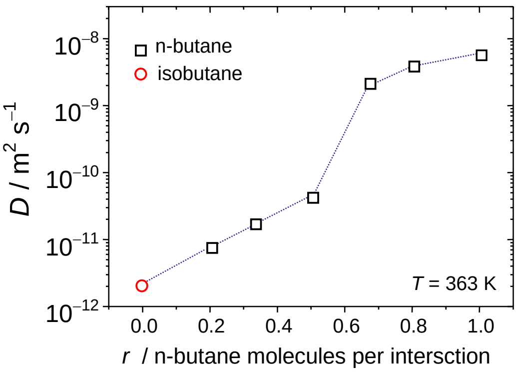

Fig. 1 Experimental data on self-diffusion coefficients of nC4 in nC4/iC4 mixtures in MFI at 363 K as a function of the loading of nC4 in the mixture. Also shown is the self-diffusivity of pure iC4.

Diffusion in liquid mixtures of acetone with different alkanes in porous glasses (4 nm and 10 nm pore diameter) was also studied [3]. In the narrow pores one dependence of acetone diffusivity with the odd or even number of carbons in the alkane chain was found [4]. This oscillation effect in the acetone diffusion coefficient by increasing n-alkane length depends on the intermolecular interaction between the different alkanes and suggests the formation of complexes under strong confinement.

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MAS PFG NMR diffusion studies of liquid crystals and liquid mixtures confined in porous glasses

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The pulsed-field gradient nuclear magnetic resonance (PFG NMR) technique is a direct and non-invasive method for measuring self-diffusion coefficients. It has proven to be an indispensable tool of studying isotropic liquids [1] and molecules in confined geometries [2]. However, if dipole-dipole interactions are not completely averaged out by molecular motions, the NMR signals are very broad, and the free induction signals decays is very fast [3]. This limits the time available for the application of gradient pulses [4] and makes impossible measuring diffusion in liquid crystals without special line-narrowing techniques [5]. In the case of liquid mixtures confined in nanoporous materials [6] dipolar broadening deteriorates the resolution in the chemical shift scale necessary for selective diffusion measurements of mixture components. This kind of problems can be overcome by combining magic-angle spinning (MAS) with pulsed field gradients. This relatively new technique is referred to as MAS PFG NMR, see e. g. [7]. MAS implies the orientation of the spinning axes with respect to the external magnetic field at the angle of $\theta_m \approx 54.7^\circ$. In comparison with other techniques [5] this type of measurements has considerable advantages. First, the increased resolution in the ppm scale permits one to observe separately each individual group with identical electronic surroundings. Second, the longer transverse relaxation time upon MAS allows for sufficient time for the application of pulsed magnetic field gradients.

Dynamic properties of the confined nematic liquid crystal 5CB has been studied by several techniques including the Dipolar Correlation Effect [8] and Field Cycling Relaxometry [9, 10]. However, no NMR diffusion measurements were performed so far. In this work we apply for the first time the MAS PFG NMR technique to liquid crystals. The nematic liquid crystal 5CB confined in Bioran glass was studied. It was shown, that the diffusion coefficient of 5CB confined in Bioran glasses exhibit an Arrhenius-like temperature dependence with an apparent activation energy E_a^{iso} = 26.7±2.7 kJ mol^{-1} close to that in the isotropic phase. A minor discontinuity at the phase transition was observed in agreement with the results of other techniques [8-10]. The measured diffusivities however do not differ significantly from the values in bulk 5CB. It is shown that diffusion studies of confined liquid crystals permit one to get a deeper insight into aspects of anisotropic molecular interactions and the effects of confinements.

Measurements of methanol / cyclohexane-mixtures in porous glass with 7.5 nm diameter (CPG7.5) yield the self-diffusion coefficients for both compounds. A comparison with the values obtained for single-component adsorption shows that the diffusivity of methanol is by factor of 2 smaller in the confined binary mixture than in the system methanol + CPG7.5. At the same time cyclohexane has the same self-diffusion coefficient in the confined mixture and in the single component system cyclohexane + CPG7.5.

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Diffusion in mesopores during melting and freezing processes

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Phase transitions of fluids confined to mesopores often exhibit pore size-dependent shifts in the transitions. Moreover, transition pairs, like freezing and melting considered in this work, in most cases do not coincide with each other giving thus rise to a hysteresis phenomenon. The microscopic mechanisms leading to such behavior are still under discussion, and additional information about the growth process of a new phase along both transitions may appreciably contribute to a further understanding of this phenomenon. Molecular diffusivity is a sensitive probe of the geometrical characteristics of the space in which it takes place. Melting and freezing processes, occurring in pores, modify the pore-space characteristics, in turn modifying the diffusion behavior of the liquid molecules. Hence, it may be used to monitor the character of the structural changes during these transitions.

In this work, we present the study of freezing and melting behavior of nitrobenzene in mesoporous silicon (PS) with one-dimensional channels with an artificially superimposed variation of the pore size along the pore axis. The combined experiments using NMR cryoporometry [1] and pulsed field gradient NMR allowed us to correlate the amount of frozen nitrobenzene in the pores and the molecular diffusivities. In mesoporous silicon prepared to provide structural correlations [2], the diffusivities measured as a function of temperature clearly shown the effect of the correlated distribution of pores with different pore sizes. These findings have been further used to understand and analyze the data for material with a random distribution of the pores. Most remarkably, there is a well-pronounced difference in the diffusivities measured along the heating and cooling branches, revealing different distributions of the frozen domains during melting and freezing. It is also discussed that the used experimental procedure may reveal very important information on the interconnectivity of the pore space, alternatively to the approach suggested in [3].

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Probing the meso- and microstructural heterogeneity of low dense networks with dendrimer probes and NMR/MRI diffusometry

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The functionality of most food materials is determined by their meso- and microstructure. Structural characterisation at these length scales is challenging and requires the deployment of complementary microscopic and spectroscopic techniques. For porous materials with dense networks, probing the diffusion behaviour of water by NMR and MRI is an established approach for obtaining descriptive meso- and microstructural parameters.

For low dense networks, however, water is not a suitable probe, hence recently the use of macromolecular probes has been proposed. So far this approach was only demonstrated for homogeneous low dense networks. Thus we embarked on a feasibility study to explore whether this approach could also be applied to systems which display meso- and microstructural heterogeneity. As a model system we used alginate networks, which can be prepared as homogeneous gels, as well as beads which display a radial crosslink density gradient. First, a homogeneous alginate gel was prepared and characterised by probing the diffusion behaviour of dendrimer probes by NMR. By monitoring the diffusion behaviour of the dendrimer probe with a range of sizes, the mesostructural heterogeneity of alginate networks could be established. Subsequently, the diffusion behaviour of dendrimers in heterogeneous alginate beads was probed.

Quantitative imaging of moisture ingress in cereal crackers: an SPI study

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Shelf life in multi-component foods with texture contrast (e.g., crispy crackers with moist filling) depends largely on texture stability. Because of differences in water activity, Aw, migration of moisture from wet to dry components will occur. This is undesirable. A number of processes can play a role in the transmission of moisture through cereal materials: gas phase wetting (moist air); capillary transport of liquid water over the surface; and diffusion of liquid water through the cereal matrix. It is not well understood which of these mechanisms dominate under what conditions.

To image water ingress in materials with low water contents, conventional imaging methods do not suffice: the T_2's are too short. In crackers the transition from crispy to soggy occurs at an Aw of ~0.5. ^1H relaxometry revealed that in this transition the largest changes are visible at a T_2 of 125 μs. The only readily available methods, suitable to image very short T_2 components, are based on Single Point Imaging (1). SPI was sensitive enough to observe changes of water content: Crackers at Aw's from 0.15 to 1 were successfully imaged at a TD of 125 μs; contrast was sufficient to follow the transition from crisp to soggy. SPI thus provides a tool to observe changes in texture stability.

We carried out moisture ingress experiments on cube-shaped pieces of dry crackers which were exposed to humid air (Aw = 0.85). Quantitative moisture content profiles could be obtained with adequate time-resolution, and this allowed monitoring of the transition from the crispy to the soggy state in a real time manner. The quantitative profiles, which were obtained for crackers with different porosity and geometries, matched with our theoretical expectations.

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Anomalous diffusion expressed through fractional order differential operators in the Bloch-Torrey equation

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We report the use of PGSE NMR to characterize heterogeneity in the structure of Sephadex gels and an oil-in-water emulsion. We demonstrate the application of fractional order models to describe the restricted diffusion characteristic of such systems. Several recent studies[1,2] have investigated the so-called anomalous diffusion stretched exponential model – $\exp[-(bD)^{\alpha}]$, where α is a measure of structural complexity that can be derived from fractal models. In this paper we propose an alternative derivation for the stretched exponential model using fractional order space derivatives. We consider the case where the spatial Laplacian in the Bloch–Torrey equation is generalized to incorporate a fractional order Brownian model of diffusivity[3]. This treatment reverts to the classical result for integer order operations. The fractional order dynamics derived were observed to fit the signal attenuation in diffusion-weighted images obtained from Sephadex gels. We have further investigated the extent to which the fractional order model can describe restricted diffusion in an emulsion.

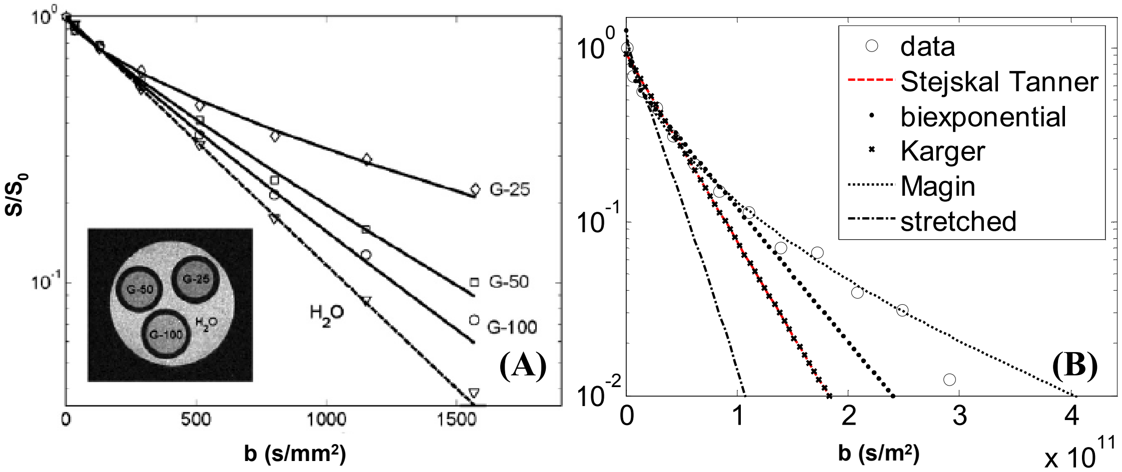

Fig. 1: (A) Normalized signal intensity plotted versus b ($b = (\gamma\delta g)^2\Delta$) for selected regions of interest in samples of distilled water and Sephadex G-25, G-50, and G-100. Experimental data were fit to the fractional order model. The inset shows a T_2-weighted spin echo image of the sample. (B) Normalized signal intensity plotted versus b for an oil-in-water emulsion. Five different models were used to fit the data. For this sample and observation time (Δ=15 s), the fractional order model yields the best fit.

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Pore-Water Interactions in Hydrated Cement Pastes by NMR

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Although cement based materials are ages old, and although they are now ubiquitous across the world, a detailed understanding of their CSH microstructure and of pore water interactions within this structure still remains elusive. To obtain this understanding is important because, without it, predictive refinement and improvement of cement properties is not possible.

In recent years, NMR relaxometry has begun to challenge the long established picture of a network of interconnected gel (~nm) and capillary (μm) pores. NMR 2D relaxometry has shown exchange of water between two reservoirs of different gel pores, has allowed measurement of the water exchange rate between them (~ms^{-1}) and has revealed a surprising lack of capillary pore water reservoir[1]. Increasingly the NMR picture is supported by numerical modelling and statistical analysis of high resolution micrographs[2].

Notwithstanding, however, the NMR results have raised a series of further questions concerning interpretation and detailed analysis of "NMR mass balance":

- Current opinion suggests that the two dominant diagonal peaks seen in 2D exchange relaxometry are associated with different size gel pores between CSH bricks of different packing density in different environments. However an alternative explanation is that rather than different pore sizes, the reservoirs can be associated with pores of similar size in regions with different Fe^{3+} impurity densities leading to different surface relaxivities. Can this alternative picture be proved or discounted?
- If the reservoirs are associated with gel porosity, then can experiments be performed to quantify the intra-CSH layer water and the bound water fraction so as to complete a detailed "NMR mass balance" and confirm the "two types of gel pore hypothesis"?
- Can the slow exchange rate (~ms^{-1}) be rationally explained if it is recognized that this corresponds to a distance of the order of microns across a nano-scale structure?
- Why can exchange not be observed in old (>months) samples?

It is the purpose of this paper to address the first two of these questions and speculate on the others. We describe a series of relaxation studies of "tailored" grey and D_2O exchanged cements to address the first question and a variable temperature double quantum filter NMR study of hydrated pastes to address the second.

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Why you can't use water to make Cryoporometric measurements of the pore size distributions in meteorites
- or in high iron content clays, rocks or concrete.

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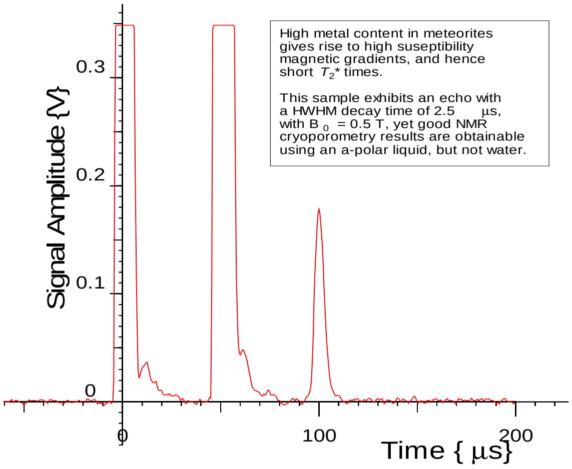
Many porous materials have high susceptibility magnetic gradients in the pores, due to the presence of iron or other magnetic materials. Thus if probe liquids are placed in the pores they exhibit fast decaying signals with a short T_2^*. Usually the actual T_2 of the liquids is also reduced, due the presence of paramagnetic ions in the pore walls.

The usual solution in NMR is to measure an echo (or echo train) at short times. However recent work (Ref. 1.) has shown that water/ice systems near a pore wall form rotator phase plastic ice, with T_2 relaxation times in the region of 100 to 200 ms. Thus if a NMR Cryoporometric measurement is attempted with a measurement time significantly less than 1 or 2 milli-seconds, the result is make a measurement based on the phase properties of the brittle to plastic ice phase transition, not that of the brittle ice to water phase transition. This gives rise to artefacts of small pore sizes that may not actually be present. This work successfully uses a-polar liquids instead.



High metal content in meteorites gives rise to high suseptibility magnetic gradients, and hence short T_2* times.

This sample exhibits an echo with a HWHM decay time of 2.5 µs, with B_0 = 0.5 T, yet good NMR cryoporometry results are obtainable using an a-polar liquid, but not water.

Fig. 1: NMR Spin-Echo from an a-polar liquid in a Meteorite sample ALH77307. Due to susceptibility gradients, the echo has a decay time HWHM of 2.5 µs.

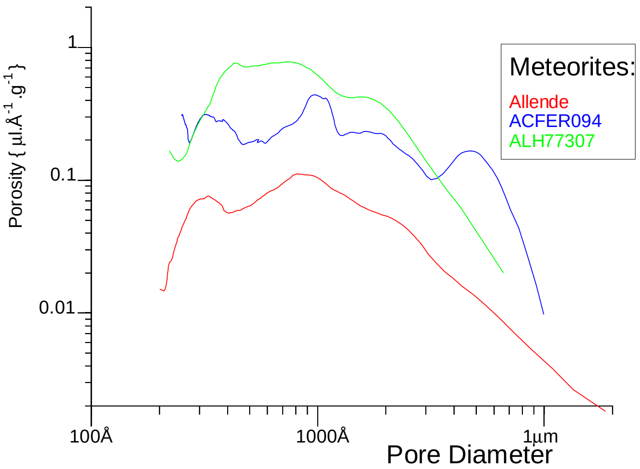


Fig. 2: Pore size distributions for 3 Meteorite samples, as measured by NMR Cryoporometry, using an a-polar liquid.

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^{1}H and ^{23}Na Imaging of Sodium Sulfate Crystallization in a Drying Porous Core

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Salt crystallization in the pore space of building materials and public works of art, such as statues and monuments, is a common precursor to cracking and subsequent decay. We have chosen sodium sulfate as our model salt to study this phenomenon because of debate in the literature about the salt form [1] which precipitates, and the practical importance of this salt in the decay of porous materials.

Sodium sulfate is an attractive salt for MRI studies because of the possibility of undertaking both ^{23}Na and ^{1}H studies to identify and discriminate the various forms of crystalline sodium sulfate, from solution. In the case of ^{1}H, we rely on the large volume fraction of water incorporated into the hydrated salts at room temperature solubilities, yielding solid like ^{1}H signals. The three crystalline forms of sodium sulfate are $Na_2SO_4.10H_2O$ (mirabilite), anhydrous Na_2SO_4 (thenardite), and $Na_2SO_4.7H_2O$ (heptahydrate). The hydrated salts yield transverse ^{23}Na lifetimes, which are less than 75 μsec at 7 Tesla, short lived, but still possible to visualize in a SPRITE experiment.

The hydrated salts yield ^{1}H transverse lifetimes, which are similarly short lived at 2.4 Tesla, but with a Sinc-Gaussian lineshape for the mirabilite. Quantification of the solution and solid component signals relies on fitting the solid and liquid decay terms, spatially resolved, for both the ^{23}Na and ^{1}H experiments with a variable encoding time in a centric scan SPRITE profile experiment. The minimum encoding time was 11 μsec.

One-dimensional experiments on a partially sealed core of calcium silicate, saturated with a solution of sodium sulfate, were undertaken with controlled drying in a temperature and humidity controlled drying chamber. The ^{1}H and ^{23}Na experiments show increased crystal deposition near the drying face. The imaging results are temperature dependent, since changes in solubility with temperature are readily revealed in the local solid/liquid ratio.

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Time dependent diffusion studies in partially filled nanometric and micrometric pores

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Provided that some conditions are fulfilled, diffusion measurements of liquids partially filling porous media have indicated an enhanced self-diffusion coefficient relative to the bulk phase [1, 2]. The reason for such observations is the molecular exchange process between two phases: liquid and saturated vapor. Molecular exchange means that the solvent molecules are intermittently subject to diffusion features in either phase. Translational displacements in the vapor phase are much faster than in the liquid phase and contribute to the enhancement of the effective diffusion coefficient.

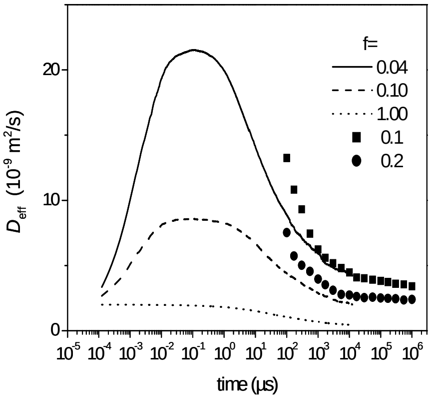

Fig.1: Measured (dots) and simulated (lines) effective (= overall averaged) diffusion coefficient versus diffusion time for different filling factors.

In our previous studies [2] the contribution of the vapor phase to molecular diffusion in silica glasses with nanometer and micrometer pores partially filled with cyclohexane (non-polar) or water (polar) was investigated for a given diffusion time (300 ms) with the aid of pulsed field-gradient NMR diffusometry. In the present investigations we are focused on time dependent diffusion coefficients. Experimental diffusion times ranging between $100\,\mu s$ and $1 s$ were probed using two unconventional NMR diffusometry techniques [3]. The experimental data were compared with Monte Carlo simulations (see Fig.1) on model structures showing a qualitatively equivalent behavior in the common time window. On this basis we could conclude that the vapor phase contribution to the effective diffusivity is particularly efficient on a diffusion time scale corresponding to root mean squared displacements of the order of pores dimension.

This work was financed by the Alexander von Humboldt Foundation, the Deutsche Forschungsgemeinschaft, and the Romanian MEC (CNCSIS 1292/2006).

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Magnetic field strength dependence of correlated Internal Gradient-relaxation time distributions in Heterogeneous Materials

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When there exists a magnetic susceptibility difference between two materials placed in an applied magnetic field, local field gradients will develop at their interfaces. These inhomogeneities in the magnetic field are referred to as “internal gradients”. The internal gradients can have detrimental effects upon experiments, leading to distorted images and inaccurate diffusion and T_2 measurements. At the same time, the dependence of internal gradients upon pore characteristics means they can provide useful information about the pore space.

Previous research has correlated T_2 with internal gradients[1]. To better understand the behaviour of internal gradients, we present here a novel NMR technique to correlate T_1 relation with internal gradients. In contrast with T_2 or the restricted diffusion coefficient, measurement of T_1 relaxation is not susceptible to the presence of internal gradients. This makes it ideal for use at high and ultra-high fields where internal gradients could potentially be significant. We observe how the distribution of T_1-internal gradient correlations in tight-packed quartz sand and Mt. Gambier limestone change at 12 MHz, 200 MHz, 400 MHz, and 900 MHz. Surprisingly, even at the ultra-high field of 900MHz there exists signal at relatively low internal gradients.

The results of the correlations provide experimental evidence to support the theory[2] that the effective internal gradients present in a sample can scale as B_0 while maximum observable gradients can scale at up to $B_0^{3/2}$. Our results also show that it is possible to reliably perform experiments on even highly heterogeneous samples at ultra high fields and that advantages come at these high fields.

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Monitoring of hydrocarbon uptake in highly conductive porous media using a unilateral NMR instrument

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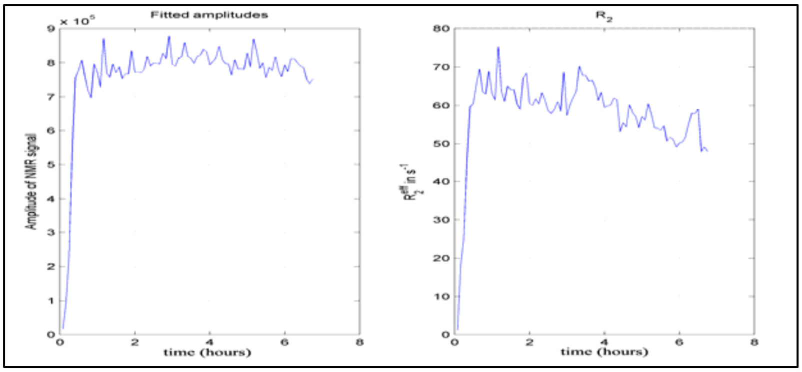
Studies of adsorption on porous media are of a great interest to the industry. Some of its characteristics can be determined by several methods such as volumetric and gravimetric measurements. A more sophisticated technique like calorimetry can be used[1] and gives information about chemical or physical adsorption. Furthermore, Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy is one of the best techniques for studying adsorption on porous material at a molecular level[2].

However, using MAS spectroscopy requires that the porous solid has already experienced adsorption prior to the real experiment. Here we show that we can monitor the time course of the uptake of an adsorbant, using a unilateral NMR instrument.

Heptane (1.5 mL) was placed in a small (i.d. 1.8 cm, L 0.9 cm) cylindrical PTFE well, on top of which a monolithic cylinder of activated carbon (see photo) was placed. The *profile* NMR MOUSE®[3] and its lift were flipped upside-down so as to monitor the NMR signal at the top of the monolith, in a slice (~400 µm x 20 mm x 20mm) 2 mm away from the instrument, overlapping with the edge of the sample.

The heptane pool evaporates within approximately two hours, whilst the NMR was monitored over more than 7 hours, allowing both adsorption and desorption to be detected.

The spin echoes were processed so as to show the time course of the effective relaxation rate (R_2^{eff}) and the NMR amplitude (see figure). A similar experiment was repeated with a less dense 'composite' of activated carbon, and with an activated carbon cloth.



We only show here the results for the monolithic activated carbon.

This work demonstrates that the uptake process of an organic compound (heptane) in an activated carbon can be successfully monitored with the MR MOUSE®, in spite of the low resistivity (565 $\Omega.m^{-1}$) of the porous material. Different NMR signatures of the uptake and desorption are seen in the three different samples, and these will be discussed.

We are currently actively focusing in trying to quantitate the signal in terms of adsorbed heptane.

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MICROSCOPIC WETTABILITY OF CARBONATE ROCKS :A PROTON FIELD CYCLING NMR APPROACH

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Nuclear Magnetic relaxation dispersion (NMRD) is strongly sensitive to the microscopic wettability of oil and brine bearing carbonate rocks. Exploring a very large range of low frequency enables isolating the typical NMRD dispersion features, $1/T_{1Surf}$, associated to the different processes of molecular surface dynamics. This allows an experimental separation of the surface and bulk microdynamics of oil and water even for a diphasic saturation of petroleum rocks. Several surface dynamical parameters such as translational correlation time, time of residence, surface affinity were determined and related to the concept of microscopic wettability of oil and water in porous media. We show our last results for diphasic mixtures (dodecane/water-brine) saturating carbonate rocks of different porosities and permeabilities when irreducible saturation of water is reached.

BLOCH-SIEGERT EFFECT IN MAGNETIC-RESONANCE SOUNDING OF AQUIFERS

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The magnetic resonance basic idea consists in reorientation of spin magnetization caused by a weak-amplitude radiofrequency field when its frequency is in resonance with the frequency with which the magnetization precesses in a strong static field. The special case of a weak field rotating around the strong field is usually used in the magnetic resonance applications while it is easily treated. F. Bloch and A. Siegert [1] studied more general case of the magnetic resonance with elliptic polarization of the radiofrequency field in particular the commonly used case of simple linear oscillation.

The magnetic resonance sounding (MRS) is a particular case of the magnetic resonance in the Earth's magnetic field as a static field $\boldsymbol{B_o}$ that is quite weak (of the order of $5 \cdot 10^{-5}$ T). Whereas the radiofrequency-field $\boldsymbol{B_1}$ produced by the surface antenna is linearly polarized and can be compatible with the geomagnetic field amplitude, therefore the effect of strong nonrotating radiofrequency field $\boldsymbol{B_1}$ can take place in the MRS. Fig. 1 exemplify a good agreement between measured data and calculated taking into account the Bloch-Siegert effect at the Ob reservoir near Novosibirsk used as a model of aquifer with known free water content (100%), depth (from 1 to 11 m under ice), and some other parameters.

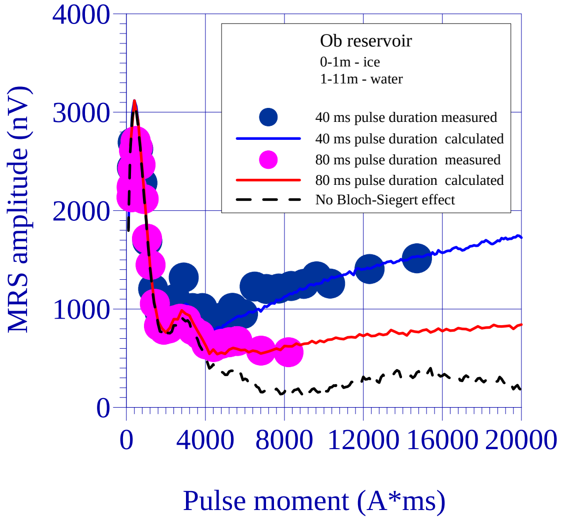

Fig. 1: The MRS amplitude vs pulse moment at 40ms and 80ms pulse durations measured (circles) and calculated (lines). Dashed line – calculated without the Bloch-Siegert effect.

Conclusion

New physical model of MRS has been developed taking into account non secular effects of spin Hamiltonian with strong and linearly polarized radiofrequency field, its experimental proof has been carried out for subice water at the Ob reservoir (modeling an aquifer).

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Internal Magnetic Field Gradients: Experimental Study

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Nuclear magnetic resonance is one of the most powerful techniques for the investigation of porous media. When the sample is placed in a uniform external field, the magnetic susceptibility difference between the porous material and the diffusing fluid leads to the appearance of non-uniform internal magnetic fields in the porous media. The inhomogeneities depend on many factors, including H_0, $\Delta\chi$ value, pore morphology and geometry. On one hand, these internal fields introduce ambiguity in the classical interpretation of NMR experimental data. On the other hand, the internal magnetic fields and their gradient distributions are determined by the porous media properties and can be used to obtain information about the porous media, the fluid condition and the localization in it [1,2].

In the present work, internal magnetic fields and their gradient distribution functions were studied by different NMR techniques, including the "tau-scanning" experiment [2]. Model (glass beads, Vycor) and natural (sand, quartz sand) porous media, fully and partially filled by different hydrocarbons, were studied. The dependences of internal field properties and their gradient distributions on different factors (pore size, diffusant molecular mobility, pore filling) were examined.

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Acknowledgements

The work was supported by RFBR No 07-03-01004 and Schlumberger Moscow.

The ^{1}H NMR R_1 of Some Hydrated Synthetic and Natural Sands

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The ^{1}H NMR R_1 of hydrated sands is important in determining the poroscity of aquifers using magnetic resonance sounding. Large R_1 variations have been reported in laboratory measurements of hydrated sands.[1] We believe these variations are attributable to the differences in the resonance frequency (ν) and mineralogy. To test this hypothesis, we measured the R_1 of fully-hydrated quartz (Sea, Ottawa, and Oregon) and synthetic (borosilicate glass spheres) sands as a function of grain diameter (d) and ν using a field cycling (Stelar FFC-2000) and 7 T high resolution (Bruker DRX-300) NMRs. Samples were cleaned, dried at 200 ºC, sieved, placed in NMR tubes, and hydrated with 18 MΩ·cm water.

R_1 data for all 28 samples displayed monoexponential behavior. R_1 values increased with both decreasing d and ν. Between $0.01 < \nu < 30$ MHz, samples displayed a linear relationship between R_1 and $\log(\nu)$, and a power law relationship between R_1 and d. The two smallest diameter sieved Ottawa sands (84 & 117 μm) displayed an order of magnitude faster R_1. EDXM (JEOL JSM-6400V) analysis revealed the presence of pyrite, probably dislodged by mechanical abrasion during the sieving and stopped by the smallest sieves. In the glass spheres and the Ottawa 84 and 117 μm samples there is a dispersion between 30 and 300 MHz caused by electron spin flips associated with the larger amount of paramagnetic material in glass and the Ottawa 84 and 117 μm samples.

Extrapolation of the R_1 vs. $\log(\nu)$ relationship allows prediction of R_1 at ν = 2.5 kHz or B_{Earth}. (Fig. 1.) Measurable R_1 differences were observed between the three natural quartz sands and glass beads. These differences can not be attributed to the geometric characteristics of the grains and porosity differences, as these were identical within experimental uncertainty. The three quartz sands had different quantities of trace paramagnetic impurities in the grains as determined by ESR (Bruker ESP-300,), which may explain the different slopes in Fig. 1.

We conclude that literature variations in R_1 are attributable to the differences in the ν of the measurements and paramagnetic impurities in the sand grains.

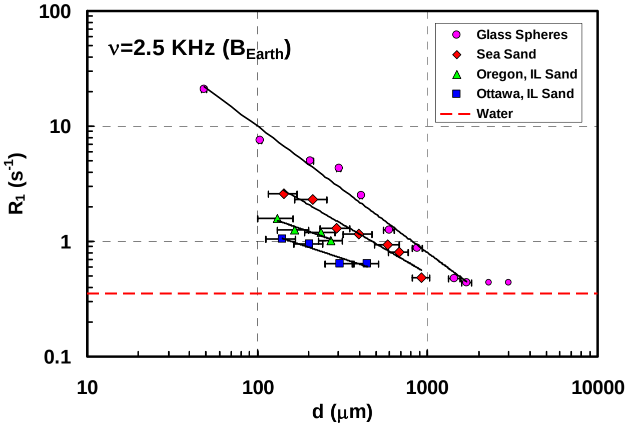

Figure 1. Predicted ^{1}H R_1 as a function of particle diameter at ν=2.5 kHz for fully hydrated, random-packed natural and synthetic sands. Solid lines are a power law fit to the data. The dashed line represents the R_1 value for bulk water. Error bars in d represent ±1σ in the range of d values for the sample. The flattening of the glass sphere data at large *d* values is attributed to a beak down in the packing efficiency when *d* approaches the diameter of the sample tube (d_{Tube}). Both the Bray[2] data at d_{Tube} = 4.5 mm and our data at d_{Tube} = 7.7 mm display this at $d > 0.22d_{Tube}$.

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^{129}Xe NMR of Xenon Trapped in Fully Dehydrated Mesoporous Silica referred to Molecular Sieves 5A and 13X

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^{129}Xe NMR techniques have been applied to probe porosity of mesoporous silica and the pore size is known to relate with the chemical shift. Since the Van der Waals radius of Xe is known to be 0.216 nm, the possible pore size to adsorb xenon should be larger than 0.4 nm in diameter. Then the mean pore diameters ranging from 0.4 to 300 nm are the possible target to show the relationship experimentally. We have developed an apparatus to produce the laser induced hyperpolarized (HP) Xe gas[1] and tried to apply it to a self-assembled porous silica sample (Lowk1), which is known as a candidate of low-dielectric constant materials for interconnects in future ultra-large scale integrated circuits (ULSIs)[2].

The temperature dependent ^{129}Xe NMR spectra were measured at the frequency of 74.7 MHz from 168 to 373 K. Since the pore size is small and the diameter is about 2 nm, the comparison was focused on materials having small pore sizes of commercial available molecular sieves 5A (0.5 nm) and 13X (1 nm). When the HP xenon gas was introduced into the samples at room temperature, the ^{129}Xe NMR signal always moved a little to the lower field side to reach an equilibrium state and the life-time of the HP xenon was shorter in 5A and 13X compared with Lowk1. The broad signal in the initial stage moved to the lower field with narrowing to approach equilibrium states, accompanied by the gradual decrease of signal intensity and the HP ^{129}Xe signal disappeared. After a little while, at the same position the ^{129}Xe signal came out and gradually the intensity increased in the opposite phase to approach to equilibrium states in intensity. Waiting about 10 min, the ^{129}Xe shift values were obtained as shown in Fig. 1. The changes in the line widths are plotted versus temperature in Fig. 2. The ^{129}Xe NMR spectra for mesoporous materials measure the averages of the residence times or numbers of xenon atoms in the mesopores under adsorbed and gas phase equilibrium at each temperature. The residence times or numbers in the mesopores vary depending on temperature and pressure, which influences the ^{129}Xe chemical shift.

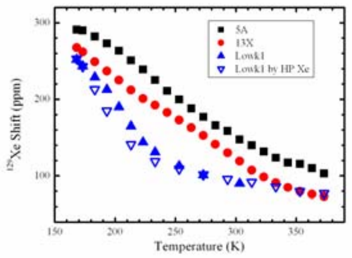

Fig. 1: ^{129}Xe shifts of 5A, 13X and Lowk1.

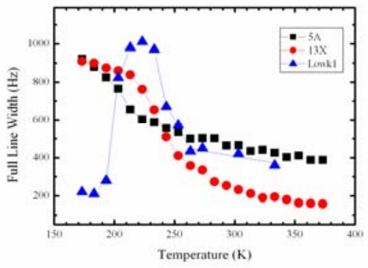

Fig. 2: ^{129}Xe full line width at half height.

A ^{129}Xe NMR study on mesoporous materials under atmospheric pressure has established. Combination of UHV treatment of the sample and the hyperpolarized ^{129}Xe NMR techniques at atmospheric pressure indicate that estimation of the size and distribution of pore by measurements of both chemical shift and line width.

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Spin-lattice relaxation of SF_6 in heterogeneous porous materials

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The spin-lattice relaxation times (T_1) of fluorine nuclei in gases such as CF_4 and C_2F_6 are known to increase considerably when the gases are confined to small pores [1]. Such behavior is expected for collisionally interrupted intramolecular interactions in the limit of extreme narrowing. As a matter of fact, the dominant relaxation mechanism for these gases is the modulation of the spin-rotation interaction by molecular collisions. In the bulk gas, T_1 is proportional to the density, as the correlation time of molecular angular momentum is determined only by the molecule-molecule collisions. In porous materials, the collision frequency is increased by the presence of molecule-wall collisions. Hence, the increase of the relaxation time may be attributed to the increase of the collision frequency [1].

A method for measuring the surface/volume ratio of porous materials by measuring how T_1 of CF_4 gas changes with confinement has recently been introduced [2]. The applicability of the method was demonstrated by analyzing samples of fumed silica (SiO_2). This material is an ultrafine powder with a high air content and very little particle-particle contact, and its surface/volume ratio can be changed by compression.

However, in most practical applications the studied material is granular. Then the analysis is complicated by the presence of voids where the gas molecules can reside. In the present work, we look for a generalization of the method to macroscopically inhomogeneous materials. To this end, we have studied the ^{19}F spin-lattice relaxation time of sulfur hexafluoride gas (SF_6) adsorbed in different types of granular porous materials.

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Imbibition delay in porous media owing to thin low permeability surface layers

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Coatings are gaining an ever-increasing importance in many technological materials, as well as in the study of the mechanisms for the ingress of water inside these materials. In a previous paper[1], fluid imbibition in rocks has been studied by Magnetic Resonance Imaging (MRI), before and after treatments to artificially change capillary and surface properties.

Using MRI, the presence of water inside each sample could be visualized and the height $z(t)$ reached by the wetting front as a function of time during experiments of capillary absorption before and after treatment could be quantified. Very good fits to the data were obtained with theoretical and empirical models of absorption kinetics, starting from the Washburn model for capillary rise, adapted to porous media instead of capillary tubes. In some cases, the model had to be modified for application to a sample having a thin low-permeability layer as a result of a treatment process. In those cases we observed some delay in the absorption for both $z(t)$ and mass absorbed, as shown in Fig. 1a and 1b, respectively. A mechanism to explain this behaviour may be the presence of a thin layer of very low permeability at the absorbing surface, and good fits to these data were obtained by introducing a delay parameter into the absorption equation. In this paper, that model has been checked on model porous media made of two rock samples of different permeabilities.

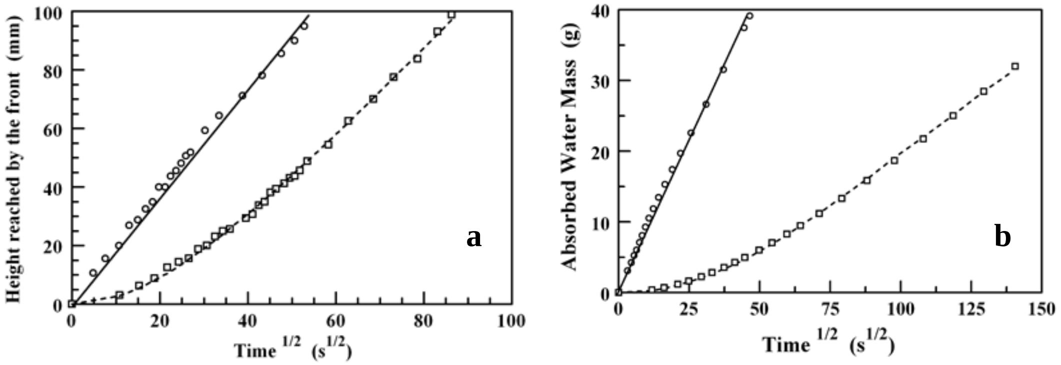

Fig. 1: Height reached by the wetting front during imbibition process (a) and total mass of absorbed water (b) as functions of square root of time for two samples. Circles and solid lines refer to an about 100 mm high sandstone sample; squares and dotted lines refer to a model porous medium constituted by the previous sample and a small, about 1 mm high, low permeability layer made of calcareous rock.

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Desalination of historical objects as studied by NMR

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ABSTRACT

Salt crystallization is one of the most important reasons for the decay of historical objects. A well known example is the historical city of Venice in which there is a lot salt decay. Reducing salt contamination is important for conservation of old historic buildings. Therefore often desalination treatments are done. The desalination of non-movable objects, like buildings, is usually made through application of so-called poultices. That is a moistened absorbent material is put on the surface of masonry. Water will than penetrate and desolve the soluble salt present. By subsequent drying the ions will be transport fror the substrate into the tpoultice. The removal of water-soluble salts sounds easy, but it can prove difficult in practice. To achieve a better poultice performance, knowledge about salt transport in the combination poultice/substrates is needed. We have studied the moisture and ion transport for various desalination systems by NMR. Based on these measurements one can categorize poultices according to their working principle of salt extraction and indicate the effectiveness for various desalination methods.

Spontaneous crystallization of meta stable sodium sulfate as observed by NMR

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Salt crystallized in pores can give rise to damage of porous materials due to existence of surface tension between pores and formed crystals. Sodium sulfate is one of the most damaging salts, but there are still many questions about its crystallization and damaging mechanisms. Especially which form of crystal will crystallize out firstly in porous media. In our experiments we have investigated the crystallization of sodium sulfate in porous building materials like fired-clay brick and in sandstone. In these experiments the crystallization was introduced by changing the temperature as the solubility of sodium sulfate is strongly temperature dependent.

Using NMR we have measured non destructively the Na concentration in these materials during crystallization. These experiments show the formation of meta stable heptahydrate form of sodium sulfate. Moreover these experiments indicate the existence of a spontaneous crystallization line. That is during cooling there is a maximum super saturation which can be reached. It was found that the type of porous material has no influence on the spontaneous crystallization line. This proves that crystallization process in these cases is caused only by the internal properties of solution. This behavior of sodium sulfate opens new questions in the understanding of crystallization damage.

High resolution MRI to probe drying and barrier properties of coatings

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In the last twenty years the environmental concerns regarding chemicals used by the coating industry has been growing rapidly. More and more coatings are reformulated and turned into waterborne systems. Still many problems concerning waterborne systems remain and new investigations and measurements techniques are required. Since the use of waterborne coatings is significantly increasing and waterborne coatings are sensitive to water it is important to investigate the connection between water transport and degradation of such coatings. In addition recently, the carcinogenicity of cobalt based catalyst was reported. Therefore alternative catalyst systems are studied for application in alkyd coatings, based on Mn or Fe. So techniques able to monitor drying of coatings and moisture transport in coatings are needed.

At present, spatial resolution nuclear magnetic (NMR) imaging is the only technique that can measure moisture transport and drying processes in coatings in-situ non-destructively with sufficient high resolution (~ 5 μm) [1]. The principle of NMR is based on the resonance of nuclei at a specific frequency that is proportional to the magnitude of the magnetic field. If this field is inhomogeneous, nuclei in different positions will resonate with different frequencies enabling imaging. By following the so-called GARfield approach (a specific design of the magnet poles) [2], the desired field gradient (in our case 36.4 T/m) and spatial resolution is obtained.

MRI probes the cross linking of the coating film by changes in polymer mobility, which decreases with increased cross linking. The results of studies on alkyd coatings indicate that the drying dynamics with cobalt as a catalyst is different from those with manganese based catalyst. In case of cobalt a cross linking front movement proportional to $\sqrt{t}$ was observed [3], whereas this was not observed in case of the manganese based catalysts, not even at high concentrations.

In addition studies have been made in which high resolution MRI shows the absorption of a solvent borne coating by an underlying porous substrate. For solvent borne coating the absorption is higher than in case of a waterborne coating, in which only the water is absorbed. Also, NMR imaging is able to distinguish different layers, measure moisture transport, measure swelling and/or shrinkage, and fluorine distribution [4].

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The formation of meta-stable sodium sulfate heptahydrate during drying in porous media as studied by NMR

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Salt weathering is a major cause of deterioration of porous building materials. Of the salts responsible in practice, especially sodium sulfate is seen as very damaging. However many questions arise concerning which sodium sulfate phase will crystallize out during salt weathering. In this study we focused on the crystallization during isothermal drying of a sample saturated with a sodium sulfate solution. As the material is drying moisture will leave and hence the salt concentration will rise until the maximum solubility is reached. From that point on crystals will be formed. Using NMR we have measured quasi simultaneously both the moisture and Na profiles during drying. These experiments have been performed at various temperatures and concentrations. In our NMR experiments we observe the formation of a metastable phase of sodium sulfate, the heptahydrate crystals.

Impact of multi-scale moisture transport on durability of hardened cement pastes

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Improving sustainibility 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 3nm 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 $T_{1\rho}$ 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.

Molecular dynamics of ionic liquids confined in solid silica matrix for lithium batteries

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Ionic liquids are known for their high ionic conductivity and their wide electrochemical potentialities. They have recently been used as electrolytes in solar and fuel cells [1, 2] and lithium batteries [3]. For such applications, these ionic liquids have been immobilized in a solid matrix [4, 5]. 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 bis(trifluoromethylsulfonyl)imide) [BMI][TFSI] as an anion-cation 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). In a first step, we have measured the proton nuclear magnetic relaxation dispersion (NMRD) of the confined proton-bearing cation [BMI]. The frequency dependence of $1/T_1$ behaves as a power law, $1/T_1 \sim \omega^{-1/2}$, over more than three orders of magnitude. This suggests a very slow decay of the intramolecular dipolar fluctuations of this confined cation at proximity of the pore surface. Such a power law remains over a very large range of temperature (10°C-70°C). This suggests a translational diffusion process at proximity of the pore surface. Several dynamical parameters have been determined from these proton NMRD such as: translational correlation time, activation energy as well as a surface diffusion coefficient that is similar to the one determined by quasi-elastic neutron scattering [6]. Moreover, we have observed a modification of the diffusive regime above 300K in conformity to recent conductivity measurements [5]. An estimation of the length of persistence associated to an average radius of curvature of the pores has been reached from the cross-over to a frequency independence of $1/T_1$ observed at low frequency. Last, we show the ^{19}F NMRD of the proton-free anion [TFSI] and obtained a power-law behaviour almost similar to the protons. This is in favour of a very-correlated dynamical motion of the anion-cation pair at room temperature within the solid and disordered silica matrix. Both the methods and the theories presented here can be applied more widely to other conducting porous media.

This work is supported by the Agence National de la Recherche ANR-06-NANO-003

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Surface Diffusion in Catalysts Probed by APGSTE NMR

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The performance of heterogeneous catalytic processes is closely linked to the access of reactant molecules to active catalytic centres on the surface. It therefore follows that the successful operation of catalytic processes relies on a fundamental understanding of molecular diffusion in heterogeneous catalysts. We have recently developed the experimental protocol to measure chemically-specific surface diffusion coefficients using Pulsed Field Gradient (PFG) Nuclear Magnetic Resonance (NMR) techniques. While the study of diffusion phenomena with PFG NMR techniques evolved in the 1960s and is nowadays part of the standard NMR toolbox, our approach allows us to quantify both the self-diffusion coefficients of molecules in a surface layer and the bulk pore liquid of a porous medium using the 13-interval APGSTE pulse sequence as outlined by Cotts [1]. For this it is necessary to acquire signal with a large number of scans at high gradient strengths of up to 1200 G cm^{-1} to assess the surface layer diffusion coefficient which is typically one to two orders of magnitude slower than the corresponding bulk liquid diffusion coefficient.

We have used this method to study solvent effects in the hydrogenation of methyl ethyl ketone (MEK) in porous 1 wt% Pd/Al_2O_3 catalyst trilobes and 1 wt% Ru/SiO_2 catalyst pellets. Water has been reported to have a significant impact on reaction rates during carbonyl hydrogenations [2-4]. Consequently we have assessed surface layer and bulk pore liquid diffusion coefficients of MEK in mixtures with two solvents – water and isopropyl alcohol (IPA) – across the entire concentration range (0-100 mol% water) under non-reacting conditions. The comparison of these results with the reaction rates of MEK at these ternary mixture compositions will be presented. The data will be used to suggest hypotheses for the role of the solvents in this hydrogenation reaction.

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Kinetics and Microstructure of Hydrating Plasters

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Gypsum ($CaSO_4 \cdot 2H_2O$) is widely used in the construction industry; it can be prefabricated into wallboards for interior wall and ceiling applications, and is sold as "plasterboard." There are two varieties of plaster, α and β, produced by wet or dry methods respectively, which can be hydrated to form solid gypsum products. The two forms of plaster differ in their reactivity with water and in the mechanical properties of the hydrated products [1]. ^{1}H NMR provides non-destructive methods of probing the microstructure of construction materials (e.g., cement [2]) continuously during hydration. This work is part of a broader study investigating improvements to the mechanical properties of set plaster under conditions of high relative humidity.

We present a comparative study of the two different types of plaster using various NMR techniques. Only the β form has been investigated in depth previously [3, 4]. NMR T_2 relaxation and imaging are used to compare the hydration kinetics and microstructural changes that occur during the hydration of the two different types of plasters. We observe a distinct difference in the hydration kinetics, as illustrated in Fig. 1, for the α- and β-plasters with a water-to-plaster ratio of w/p = 1. The α-plaster starts hydrating immediately following the addition of water, whereas the hydration of β-plaster is characterised by a long induction period. The β-plaster hydrates much faster, although the time required for both plasters to reach the same residual water content is similar.

We have also examined the hydration kinetics, microstructure and morphology of the gypsum crystals as a function of w/p ratio and inclusion of additives. The NMR study is supported by X-ray Microtomography data, which will also be presented.

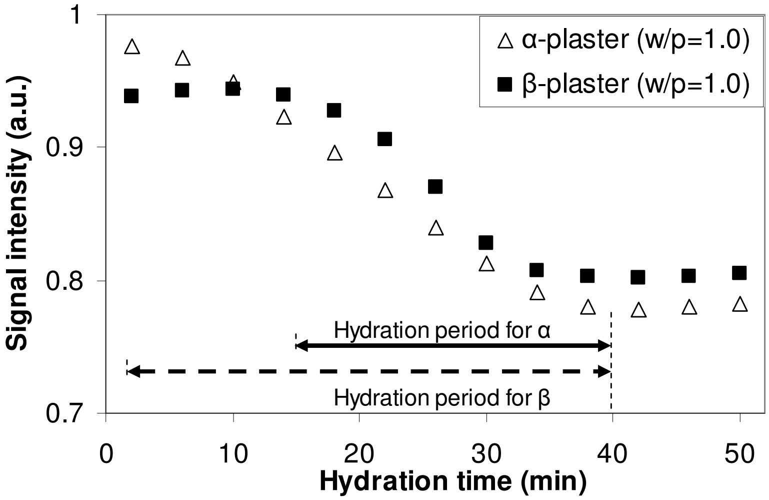

Fig. 1: Variation of average signal intensity from 1D profiles of two different plasters during the hydration.

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Understanding T_2 relaxation times in hardening cement pastes using the NMR exchange and the Powers' hydration models

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Transverse relaxation times (T_2) of physically bound water in cement pastes decrease monotonously from values of about 10 ms to 20 ms observed in freshly mixed glutinous cement pastes down to less than 1 ms in the hardened cements [1-3]. These T_2 changes occur during the first day(s) of cement hydration and are qualitatively rationalized by the decreasing pore sizes due to the growth of solid calcium silicate hydrate (CSH) phases.

The Powers' model of cement hydration [4] assumes that changes of macroscopic properties of the cement pastes due to hydration may be described by interrelated changes of the volume fractions of the unreacted cement, the capillary water, the solid hydration products and the gel water. Among these volume fractions, the capillary and gel water can be observed by low-field ^{1}H NMR relaxometry. However, CPMG NMR studies with ordinary white and Portland cement pastes show only one peak in the T_2 relaxation time distribution, which means that it is not possible to distinguish between the gel and capillary bound water fractions using expected differences in their T_2 relaxation times. Thus, there must be a fast exchange between both water fractions on a microscopic scale, which allows one to observe only an effective, averaged relaxation time in CPMG NMR.

The NMR two-site fast exchange model allowed us to predict the effective relaxation rate ($1/T_2$) from the relaxation rates of the gel ($1/T_{2,gw}$) and the capillary ($1/T_{2,cw}$) bound water fractions and their relative amounts in the cement paste. Using the Powers' model, the required relative amounts can be replaced by the initial water-to-cement (wc) ratio and the degree of cement hydration (α) yielding:

$$\frac{1}{T_2} = \frac{0.19 \cdot \alpha}{wc - 0.23 \cdot \alpha} \frac{1}{T_{2,gw}} + \frac{wc - (0.23 + 0.19) \cdot \alpha}{wc - 0.23 \cdot \alpha} \frac{1}{T_{2,cw}}$$

This equation is found to be in excellent agreement with experimentally determined relaxation times measured in hydrating white and Portland cement pastes of different wc ratios over a period of two days after cement paste preparation. Since the NMR measurements are also used to determine the degree of hydration (α), the relaxation rates of the gel ($1/T_{2,gw}$) and the capillary ($1/T_{2,cw}$) water fractions are the only adjustable parameter in this approach. Thus, they may be used in future NMR studies to characterize different cement mixtures and the cement hydration under the influence of additives changing, e.g., the water available during the hydration reaction.

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Analysis of a Novel Ceramic Pore Structure using PGSE NMR

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Ceramic pore structures produced by a novel tape casting method suggest the opportunity to optimize porous transport properties for application in a variety of industrial sectors; e.g. fuel cells, filtration, etc. [1]. Magnetic Resonance Microscopy techniques have been used to probe the nature of these ceramic pore structures. Spatially resolved pulsed gradient spin echo (PGSE) techniques were used to obtain displacement propagators of pressure driven octane flowing through a tape cast ceramic sample. The displacement distributions suggest anomalous (non-Gaussian) transport of octane through the ceramic structure. In addition, spatially resolved PGSE techniques were used to observe the pore structure induced restricted diffusion of no-flow octane. The impact of restricted diffusion on the signal attenuation clearly demonstrates both the one dimensional affine scaling of the average pore dimensions and the quasi-elliptical transverse pore shape, see Figs. 1 & 2.

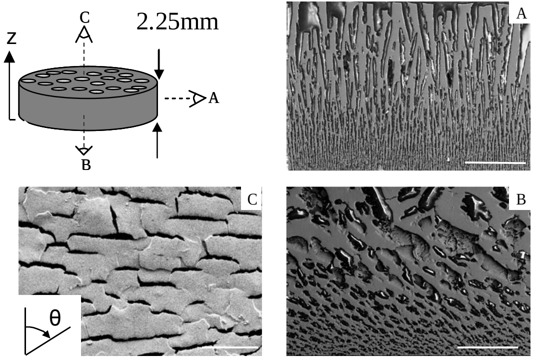

Fig. 1: SEM image of tape cast ceramic, bar=400μm

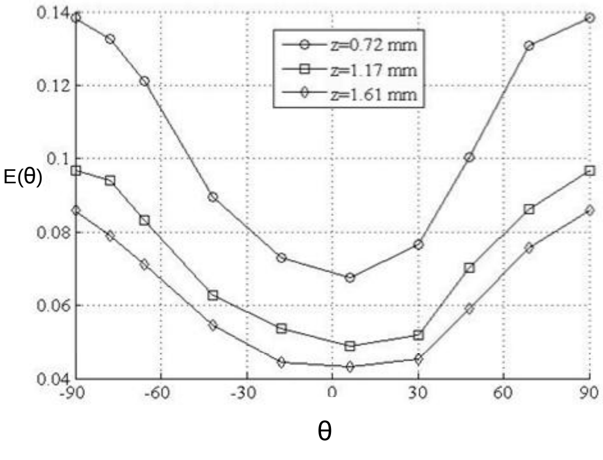

Fig. 2: PGSE signal attenuation of stationary octane saturating a tape cast ceramic as a function of longitudinal position and gradient vector orientation, constant **q**

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Ion and polymer mobility in swelling hydrogels

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The possibility for applying hydrogels as sensors and actuators is to a large degree dependent on the feasibility to generate fast responses to a range of different external stimuli; these can be temperature, pH value, or ion concentration in a solvent. The response is commonly expressed in swelling or shrinking of the gel, where volume changes of two or three orders of magnitude have been observed. Such hydrogels can then be used e.g. as drug release carriers, valves, filters or mechanical switches. In most cases, hydrogels represent a porous mesh constructed of chemically cross-linked polymer chains, but additional macroscopic porosity can be superimposed into the gel matrix.

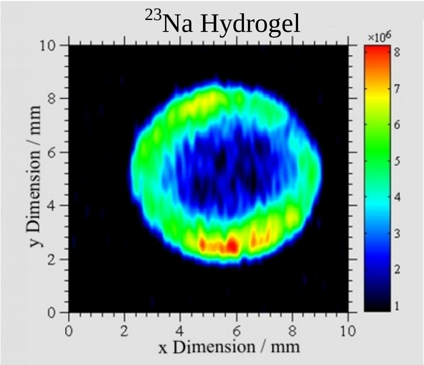

Fig. 1: ^{23}Na Spin-density MRI of Poly-(Na acrylate) Hydrogel

The fast swelling response in ionic hydrogels, of which poly(Na acrylate) is a prominent example, is due to the osmotic pressure difference caused by the concentration of ions inside and outside the hydrogel matrix. In the presence of water the carboxylic groups of the polymer backbone will dissociate, adding a supplementary swelling force by repelling each other. The swelling parameters can be controlled by the crosslinker concentration and the charge density which both influence the mechanical properties. Hydrogels with a small amount of crosslinker possess an increased mobility of the polymer backbone and are able to imbibe large volumes of water. Furthermore, foreign ions like calcium, magnesium and aluminum will replace the sodium ions present near the carboxylic groups. Because of the bivalency character of these ions, they restrict the mobility of the polymer backbone, while the osmotic equilibrium is partially destroyed affecting the swelling properties. The dynamics and concurrence reactions between the sodium and the foreign ions inside and outside the hydrogel matrix are not sufficiently understood. This understanding is fundamental to control the swelling parameters.

In order to investigate the swelling response and the polymeric and ionic dynamics, a series of polyacrylate hydrogels partially neutralized with sodium hydroxide and dried over a lyophilized process were prepared. The concentrations of the crosslinker as well as of the ions in solution were varied systematically, and ^{1}H and ^{23}Na relaxation, diffusion and imaging experiments were carried out. In this work we report on the dependence of the sodium dynamics within the pore space of the hydrogel, and provide real-time ^{23}Na microscopic images during the swelling and drying processes that allow quantification of the spatially dependent backbone and ion mobility as a function of external stimuli.

Time evolution of the “Solid” and “Liquid” ^{1}H signals during cement paste hydration

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NMR Relaxometry of ^{1}H nuclei has been widely applied to cement pastes during hydration, and models have been presented to interpret the experimental data. In this study we used a particular kind of data computation, to follow the changes of freshly prepared cement pastes, starting from the beginning up to many hours and days after the preparation. The method consists in the quasi-continuous T_1 distribution analysis of proton signals, after “Solid” and ”Liquid” signal separation, as described below.

As well known, many sample materials give both “Solid” signal components, from protons of low mobility, and also “Liquid” components, from protons with higher molecular mobility. The “Solid” gives a very fast FID decay that in a log-signal plot is initially quadratic in time (initially approximately Gaussian), while the “Liquid” gives initially exponential decay. In the course of time we settled on an algorithm (T_1-Filter) to filter the FIDs obtained at different Inversion Recovery times in IR experiments able to give estimates of four parameters: Tg, the time constant of a Gaussian with the same initial log-FID curvature, X2, its corresponding extrapolated amplitude, T2_FID, the T_2 corresponding to the initial slope of the “Liquid” component, and X1, its corresponding extrapolated amplitude. The Solid/Liquid amplitude ratio, X2/X1, is also calculated. Special attention has been devoted to avoiding the introduction of excessive scatter in the computed results, by forming stacks of FIDs on which computation were made, and to take into account the eventual changes in the FID slopes of the “Liquid” component with Recovery time, due to possible T_2 multi-exponential decays. In such a way we were able to get separate files for input to our multi-exponential inversion software (UPENWin)[1] for both “Solid” and “Liquid”, with an accurate determination of the two signal amplitudes at each Inversion Recovery time.

We have observed the two components (“Solid” and “Liquid”) in many biological samples, bone, wood, cartilage, collagen. Also cement pastes during hydration show the two components, that we have studied by using the four parameters described above and by quasi-continuous T_1 distributions of both components.

The distributions vary very quickly and are clear markers of the rapid changes of the cement pastes in the first few hours after preparation. As a new result, we found that the parameter X2/X1 changes drastically in the first hours and takes days to reach a plateau.

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Time-dependent diffusion coefficient of proton in perfluorosulfonated membrane

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The perfluorosulfonated membranes have attracted much attention in the past decade because of their applications in polymer electrolyte fuel cells (PEFC). However, little is known about pore structure in long-range order (submicron) when resolving the detailed transport mechanism relevant to the proton conductivity. In this study, we focused on probing the pore structure of submicron size of three-dimensional structure of the polymer membrane by means of observation of the time-dependent diffusion coefficient, $D(\Delta_{eff})$, of proton. Diffusion measurements were carried out by two kinds of pulse sequences, oscillating gradient spin echo (OGSE)[1] and bipolar gradients with a longitudinal eddy delay (BPPled)[2]. Nafion 117 was used as a perfluorosulfonated membrane. The water content of the sample was controlled in a humidity chamber (r.h.=50%) or with saturated aqueous solution of K_2SO_4 (r.h.=97%). The resulted water content was estimated dry and wet membrane weight.

Fig. 1 shows the $D(\Delta_{eff})$ in the perfluorosulfonated membrane with 6 and 24% of water contents at various temperature from 233 to 308 K. The diffusion coefficients in $\Delta_{eff}>30$ ms indicated a constant value regardless of water content and temperature. On the other hand, the diffusion coefficients in $\Delta_{eff}<2$ ms were remarkably changed at low temperature. This tendency was more pronounced with 6% of water content. It was suggested that the pore structure with lower water content have pathways with restricted geometry for proton transport. To evaluate the surface-to-volume ratio of pore, we applied Mitra equation[3] to $D(\Delta_{eff})$ of the perfluorosulfonated membrane with 6% of water content at 233K. A magnitude of restricted space for proton diffusion could be evaluated as hundreds nanometers, which was clearly larger than well-known water domain size, about several nanometers. We think that it is likely to reflect superstructures originated from clustering of semicrystals observed via ultra small angle neutron scattering[4].

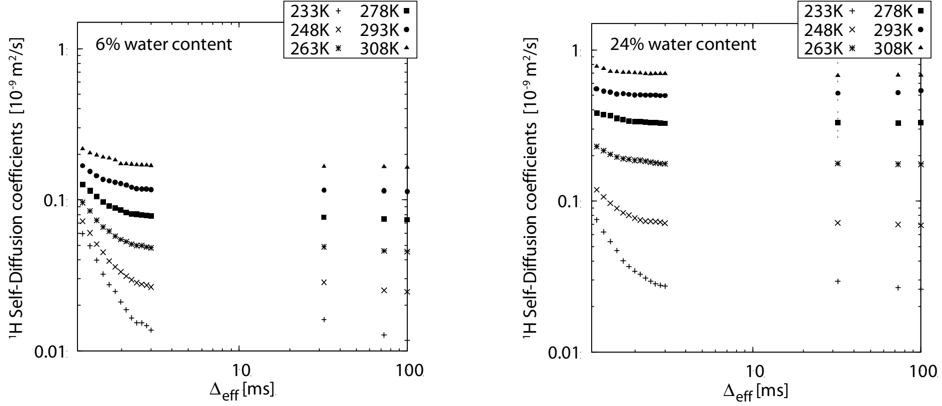

Fig. 1: Time-dependent diffusion coefficients of proton in N117 with 6 and 24% of water content at various temperatures.

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Liquid Crystals Constrained in Thin Film Capillary Investigated by DHK Spin Echo SPI Measurements

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Liquid crystals are anisotropic fluids and it is well known that self-diffusion behavior can provide valuable information on the molecular assemblage in liquid crystal phases [1]. Nuclear magnetic resonance is a well-established technique to study orientational order and dynamics of liquid crystals in porous media [2]. In this work we present a study of liquid crystal properties in constrained thin film capillary (thickness ~ 200 μm) at different temperatures. The liquid crystal under study is the common N-(p-methoxybenzylidene)–p –n –butylaniline (MBBA). Its nematic phase extends from 20°C to 43°C in bulk.

Translational self-diffusion measurements have been performed in the mesophases of MBBA liquid crystal by means of pulsed field gradient approach as a function of temperature in the nematic and isotropic phases. We found that in the isotropic phase the diffusion coefficient is not a simple scalar quantity and it has orientational dependence due to the constraint of the capillary wall ($D_{zz}/D_{yy} \approx 7.3$). To characterize the diffusion distribution of liquid crystals within the thin film, a double half k (DHK) spin echo single point mapping (SPI) diffusion mapping experiment was performed using a parallel plate RF probe. The method provides accurate diffusion tensor measurements with pixel resolution of 4μm.

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Application of low field and solid-state NMR spectroscopy to study the liquid/liquid interface in porous space of clay minerals and shales

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The study of complex multi-component systems such as liquid/liquid/mineral interactions in porous space of clays and shales is a challenging task. In petroleum research understanding displacement, redistribution, adsorption of oil and water plays an important role in considering: (i) oil production (ii) the problem of reservoir top seal, and (iii) environmental considerations.

The samples, minerals, clays and shales, were prepared in the form of powder to simplify the process of liquid saturation and crude oil treatment. The preliminary screening of the samples using optical/fluorescence and scanning electron microscopy and XPS revealed differences in wetting behaviour of the samples. Several NMR methods were applied to characterise these systems: oil and water phases competing for mineral surfaces. The liquid/liquid displacements and distribution within porous medium as studied with the “Maran Ultra-2”, T_2 were up to 10000 ms. The oil interaction with the mineral surfaces does affect the oil mobility, T_2, values only up to 100 ms. Using a combination of Bruker NMR Surface Analyser MOUSE (15 MHz proton resonance), NMR Minispec (20 MHz), and the solid-state NMR (300MHz) we were able to investigate surface-adsorbed hydrocarbons.

The detailed NMR analysis shows that the process of liquid/liquid displacement can be characterised and analysed considering the relaxation times and signal amplitudes. The results from low field NMR measurements are in good correlation with the solid-state data, where the changes of oil dynamics in the solid matrix were correlated to the different crude oils and different shale composition – variable hydrophobicity. All in all the NMR results were found to correlate well with other data and they have been consistent so we could consider a combination of low and high-field NMR spectroscopy as a tool of choice for investigating shale and clay wettability.

PFG-NMR and Goldman-Shen study of water diffusion and cross-relaxation in Polyelectrolyte Multilayers

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The self-assembly of polyelectrolytes of alternating charge from aqueous solutions onto charged surfaces leads to the formation of multilayered films. Their permeation properties for different types of molecules and their porosity are of general interest[1-3], since the multilayers can act as separation membranes or colloidal hollow carriers. A direct determination of diffusion coefficients of small molecules within and through the multilayers is attractive, but hard to achieve for nanometer thin films.

Here, we study free-standing films, which are densely stacked to achive a high filling factor, and subsequently equilibrated at different relative humidities. We investigate the diffusion of water molecules in a film of poly(styrene sulfonate)/poly(diallyldimethyl ammoniumchoride) by means of Pulsed-Field-Gradient-NMR. A non-Gaussian diffusion behaviour is found, which strongly depends on the relative humidity. Furthermore, a pronounced dependence of the PFG echo decay on the diffusion time is observed, which might suggest restricted diffusion in a porous structure. However, an evaluation in a model of restricted diffusion does not lead to conclusive results. Therefore, a potential influence of cross-relaxation between water and polymer ^{1}H spins is investigated by a Goldman-Shen pulse sequence. The data are analysed in a model established for cross-relaxation in polymer hydrogels[4,5], which yields cross relaxation rates. These are of an order of magnitude relevant in the interpretation of diffusion echo decays, which leads to a re-interpretation of the diffusion data.

From both the diffusion and cross relaxation experiments it can be concluded that the dynamic behavior of water in polyelectrolyte multilayers is highly dependent on the water content.

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Time dependent NMR spectroscopy on ionic ferrofluids

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Magnetic nanoparticles colloidally suspended in a ferrofluid exhibit a tendency to form clusters and chain-like structures under the influence of an external magnetic field [1-7]. Its behavior resembles a liquid in a porous media. Recently we used Raman spectroscopy to monitor the metastable cluster formation and its dynamics in surfacted and ionic ferrofluids [5-7]. In this work we present results of a complementary study of the magnetic-field induced behavior of a water-based ionic ferrofluid (IFF) with a concentration of 1 vol.% using nuclear magnetic resonance (NMR) spectroscopy. For the measurements we used a low-resolution NMR spectrometer working at room temperature with a homogenous magnetic field of 400 mT.

In the experiments, an electrostatically stabilized ferrofluid which has not been exposed previously to any magnetic field is placed at 300 K in the bore of the NMR spectrometer. The NMR spectrum displays an asymmetric feature which is composed by two peaks of different intensity (Fig.1). The main peak is blue-shifted by approximately 17 kHz from the resonance frequency of “pure and free” water molecules [8]. The less intense peak appears to be centered at around 3 kHz above the pure water frequency. Both peaks are attributed to two different dynamic environments of water molecules in the ferrofluid [8].

Figure 2 shows the time evolution of the peak amplitude of both peaks in a time scale of more than one hour. The amplitude of the NMR signal of the 17 kHz feature exhibits a slight increase in the first 300 s followed by a strong reduction in intensity, reaching its minimum after approximately 15 min. Simultaneously, the amplitude of the 3 kHz peak corresponding to the NMR signal stemming from water molecules far from the magnetic nanoparticles increases monotonically, saturating at times longer than one hour. This contrasting behavior of both NMR signals is readily understood by considering the dynamical processes within the ferrofluid triggered by an external magnetic field, as revealed by Raman spectroscopy [7].

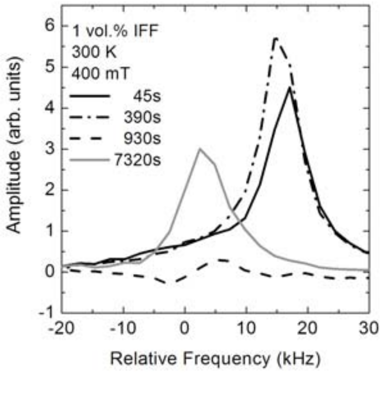

Fig.1 NMR spectra of an ionic ferrofluid at different times in a magnetic field of 400 mT.

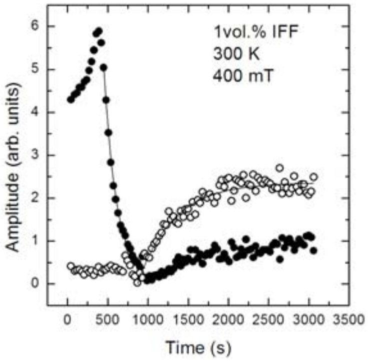

Fig.2 Time evolution of the amplitude of the 17 kHz (solid points) and the 3 kHz (open symbols) NMR peaks. Lines are fits using simple exponential functions.

TD-NMR investigation of the effect of curing-temperature on the hydration and porous microstructure development in cement

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Time-domain NMR experiments can be implemented using an instrument with low-field magnet. This makes implementation of fast quantitative material characterization combined with portability, possible. The hydration and porous microstructure development in cement during curing is key to its structural attributes. How the ambient temperature during the curing process of cement, of various types, affects these processes, is investigated in this work through time-domain NMR. Variable temperature NMR relaxation and diffusion measurements were utilized to look into the hydration kinetics and the evolution of microstructure during the curing process. All these measurements were done with probes tuned to the Hydrogen nucleus, and thus looking at the change in mobility and diffusion characteristics of water molecules present in the curing cement system. The NMR data will also be supported by IR-imaging results. This research work will be helpful in non-invasive, fast, and quantitative assessment of proper curing conditions (e.g. temperature) for a specific type of cement, as well as predictive mathematical model development of the process.

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Methodical aspects of 2D NMR spectroscopy under conditions of ultra-high pulsed field gradients

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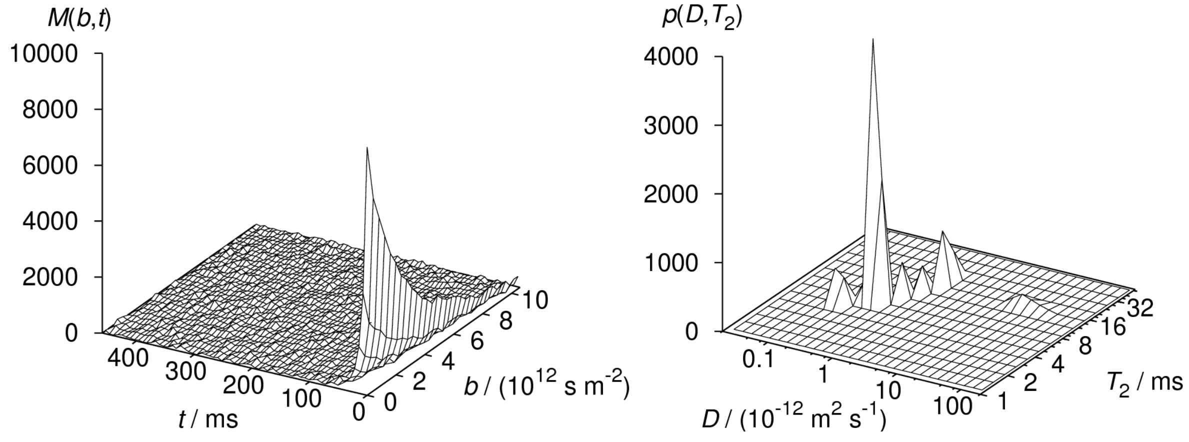
Multidimensional NMR correlation experiments based on an inverse Laplace transformation (see e.g. [1]) have been established as a powerful tool for the investigation of material structure and properties within the last few years. We successfully combined these recent methods with ultra-high pulsed magnetic field gradients of up to 35 T/m [2], which allows us to correlate molecular displacements in the order of 100 nm with NMR parameters, such as relaxation time T_2.

Basic concepts for the handling of ultra-high pulsed field gradients were adapted accordingly. This concerns in particular the introduction of a read gradient at suitable positions of the pulse sequences as well as the development of a script automating the steps taken during the experiment. The software interface controlling the NMR experiment ensures the detection of mismatched pulsed field gradients and their subsequent correction as proposed in [2].

However, an additional requirement for experiments involving the inverse Laplace transformation for data processing is to attenuate the NMR signal down to a signal-to-noise ratio of about one. This demand tends to let the aforementioned detection of gradient mismatches fail for evanescent signals. We overcame this challenge by the introduction of a termination condition. Hence, the NMR measurement is terminated, if the signal is attenuated below a predefined signal-to-noise ratio and/or if the pulsed field gradient matching procedure returns unreasonable values.

First experiments were successfully applied to several lubrication oil samples with distributions of diffusion coefficients and NMR relaxation times (fig. 1). Please note the small diffusivities and short T_2 which indeed require short and ultra-high pulsed field gradients.



(a) NMR signal map

(b) Inverse Laplace transformation of (a)

Fig. 1: Diffusion-Relaxation correlation experiment with lubricating oil at T=340 K

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Two–dimensional Laplace inversions applied to multi–component T_2–T_2 exchange experiments

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The two-dimensional (2D) T_2-T_2 molecular exchange NMR experiments with a period of magnetization storage between the two T_2 relaxation encoding periods [1] are presented. A CPMG pulse sequence with variable echo number is used to encode the signal amplitude in the indirect dimension and the magnetization decay is recorded by a CPMG sequence in the directly detected dimension. The two-dimensional time map was inverted using a fast Laplace algorithm [2, 3] to obtain the T_2–T_2 exchange map. The relaxation exchange from the fast relaxing nuclei in molecules associated with pore surfaces or superficial liquid shell and the more slowly relaxing nuclei associated with molecules in the bulk liquid filling the materials pores can be observed as cross–peaks in the T_2–T_2 exchange maps. T_2–M_Z(store)–T_2 2D ^{1}H NMR *spectra*, recorded at high and low homogeneous magnetic fields of water and oil in sand, air bubbles in water and foams, exchange of liquid–foam and liquid–saturated vapors of chloroform, are presented. Systematic studies as a function of the mixing time were performed. Interesting and at the same time challenging results, from the interpretation point of view, are reported for a mixing time comparable to or smaller than the maximum duration of the CPMG pulse sequence. In the majority of cases only unidirectional exchanges, from low to high or from high to low relaxation times are observed. A clear bidirectional exchange was observed for water, the superficial liquid shell, and foam. The 2D Laplace inversion method of T_2–T_2 exchange NMR is a valuable tool to observe the motion of molecules in heterogeneous environments. Nevertheless, a quantitative interpretation of the T_2–T_2 exchange maps in the fast exchange limit is possible only using numerical simulations. The preliminary T_2–T_2 exchange NMR experiments, shows that the investigations of heterogeneous processes, like catalysis in small chemical reactors, can successfully be investigated.

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Monte Carlo simulations of the two-dimensional NMR T_2-T_2 exchange of fluids in porous media

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Classical two-dimensional (2D) NMR T_2-T_2 exchange experiments with a period of magnetization storage between the two T_2 relaxation encoding periods T_2–M_Z(store)–T_2 [1] assumes that the molecular exchange processes take place during the store period. Fast NMR experiments use the CPMG pulse sequence to stroboscopically encode the T_2 relaxation time in the indirect and the directly observed dimensions. There are numerous samples, characterized by long T_2 relaxation times, for which the relevant exchange time, associated with the storage period, is comparable to or less than the duration of CPMG echo train decay. In these cases, dynamic processes during the preparation and exchange periods can have a direct influence on the decoding of T_2 relaxation via a second CPMG sequence. In the fast exchange limit, the simplest CPMG decay can be affected by molecular exchange. The interpretation of results in the presence of rapidly exchanging relaxation is not trivial and can be done correctly only by numerical simulation of molecular dynamics. The effect of molecular exchange processes on the one-dimensional (1D) T_2 and two-dimensional (2D) NMR T_2-T_2 Laplace distributions [2, 3] were studied by Monte–Carlo simulations. A homogeneous static magnetic field is assumed, and no disturbing effects like the pore surface magnetic susceptibility is considered. A systematic study is conducted as a function of NMR pulse sequences parameters, transverse relaxation rates, time, and distribution of exchange rates. A system from free random walk molecules and excluded volume bulk molecules was considered. The difference in the dynamic behavior inside saturated and unsaturated pore is highlighted. Systems in dynamical equilibrium and non-equilibrium were also under investigation. The geometrical factor is studied for unidirectional flow, single pore bulk-to-surface shell exchange, and systems with connected pores. Particular molecular dynamics including exchange phenomena lead to particular features in 1D and 2D data. Matching the experimental data with simulated ones can be developed into a useful tool for the characterization of complex materials. For example the knowledge of fast exchange rate can provide a powerful means of characterizing the pore surface-to-volume ratio.

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Using 2D Inverse Fourier Transformation to Observe Internal Magnetic Fields and Internal Magnetic Field Gradients

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Multidimensional NMR measurements, including inverse Fourier transformation (IFT), and more recently, inverse Laplace transformation (ILT), are frequently used in separation, correlation, and exchange experiments [1]. Often these experiments allow us to obtain knowledge about a system that is otherwise difficult to attain with a one dimensional experiment.

It is well known that porous media in an applied magnetic field will experience internal magnetic field inhomogeneities due to susceptibility differences from its various components. This was first discovered by Brown [2] using ferromagnetic grains suspended in water with 5% carboxy-methylcellulose, and expanded upon by Drain [3]who examined the broadening of magnetic resonance lines in powdered samples. More recently, the internal field has been studied in more depth by Audoly [4] using a finney pack of non-penetrating spheres.

We study these internal magnetic field inhomogeneities using exchange spectroscopy with various sized soda glass bead packs in distilled water. Our experiment involves an acquisition and evolution domain each consisting of a free induction decay so that the two Fourier domains correspond to the spectral distribution of local fields. By performing the exchange experiment over several different mixing times, twe obtain 2D data from which we study the effects of changes in location of a diffusing water molecule in the presence of these internal magnetic field, using 2D IFT. We show that exchange in the internal magnetic field can be seen in a 2D IFT by peak broadening. This is potentially useful for studying the internal magnetic field gradients in more complicated systems such as sandstones or other porous media. We anticipate the extension to 2D correlation experiments involving the Fourier domain of local field and an Inverse Laplace domain [5] of internal magnetic field gradient.

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Two-dimensional NMR of Diffusion Systems

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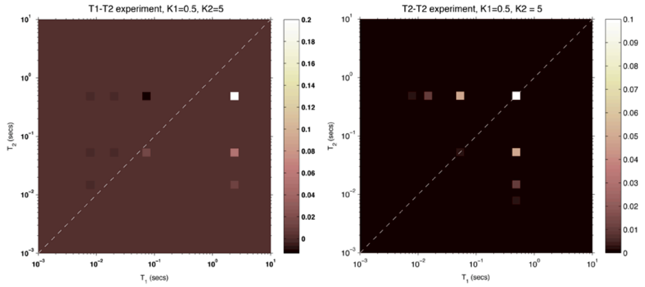
2D NMR of relaxation and diffusion is a significant advance in the study of porous materials. There have been many applications of 2D NMR as a way to distinguish signals from different phases e.g. oil, water and gases, and different geometries. 2D NMR has also been used to probe water diffusion from one pore to another. The analogy to such experiments is the conventional NOESY, the 2D NMR in frequency domain. Such experiments offer the potential to probe the connectivity of pore structures and permeability of membranes.

We show that the diffusion system itself, even within a single, shows a whole range of behaviors in 2D NMR, including the appearance of off-diagonal peaks in T1-T2 experiments (see top panels in the Figure) which have been interpreted as arising from exchange. We confirm, however, that under certain circumstances, the off-diagonal peaks become significantly enhanced by diffusive coupling between pores (see bottom panels in the Figure) and could, in principle, be used as a signature of connectivity. We study these effects within the general framework of the Torrey-Bloch formulation, which becomes the diffusion equation,

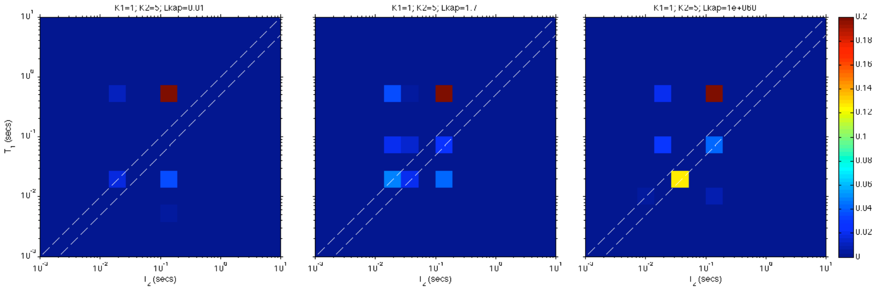
$$\frac{\partial}{\partial u} m(\mathbf{r},t) = D\nabla^2 m(\mathbf{r},t), \text{ and } m(\mathbf{r},t) = \sum_n a_n \phi_n(r) \exp(-\frac{t}{\tau_n}),$$

for the evolution of longitudinal magnetization. Here *m* is the magnetization deviation from its equilibrium, and ϕ_n and τ_n are the eigenfunctions and eigenvalues, respectively.

The spectroscopy of such an eigen system characterizes the pore space. In fact, with different surface relaxivity for longitudinal and transverse magnetization decays, two sets of eigenfunctions and eigenvalues are relevant, the longitudinal L-modes and the transverse T-modes. Each is a complete set of functions, mutually orthogonal within the set. The overlap between the L-modes and T-modes depends on the surface relaxivity. This overlap is critical for the variety of behavior of the 2D NMR results, including the appearance and intensity of the off-diagonal peaks. Though our present results are limited to one-dimensional coupled pores, our approach based on the Torrey-Bloch equation allows numerical simulations of 2D NMR for arbitrary 3D pore geometry.



Single pore, T1-T2 and T2-T2 experiments



Two coupled pores T1-T2 experiments, from strongest coupling (left panel) to weakest (right panel)

Spatially Resolved Two-Dimensional T_2-D MRI in Porous Media

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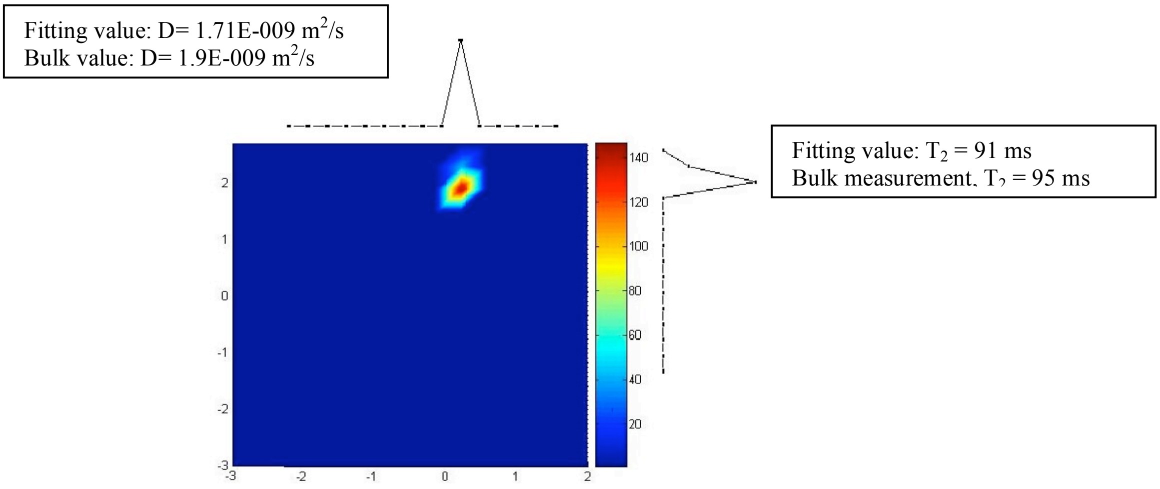
Discrimination of water and oil in petroleum reservoir exploration is a critical measurement for down-hole NMR. The most robust and successful measurements have been developed by Schlumberger and feature a 2D inverse Laplace transform to resolve the T_2 distribution, which largely depends on the pore structure and pore size distribution, from the diffusion coefficient distribution which largely depends on molecular mobility. Neither suffices in isolation to fully characterize the fluids or the medium.

In our laboratory studies of fluids in porous media, frequently reservoir core plugs, we seek a similar ability to characterize the fluids and matrix - but spatially resolved. Spatial resolution is critical for heterogeneous samples and for examination of processes that introduce a heterogeneous fluid distribution – such as core flooding.

In this work we explore a new version of the stimulated echo PFG T_2-diffusion experiment. Diffusive attenuation is modified by changing the PFG gradient amplitudes, not the stimulated echo evolution time. We add pure phase encode spatial encoding gradients in linear combination with the PFG diffusion gradients for spatial resolution of the experiment.

This simple modification of the experiment is remarkably successful, and robust, yet seems not previously to have been reported in the literature. We limit spatial resolution in core plug samples to 1 dimension in order to ensure reasonable acquisition times for the overall experiment.



Fitting value: D= 1.71E-009 m^2/s
Bulk value: D= 1.9E-009 m^2/s

Fitting value: T_2 = 91 ms
Bulk measurement, T_2 = 95 ms

Fig. 1: Single pixel T_2-Diffusion spectrum from a one dimensional phantom. Inverse Laplace transformation was undertaken with Magritek software.

We ensure short echo times and accurate gradient switching through the use of a magnetic field gradient measurement and adjustment method outlined in a separate abstract.

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Diffusional coupling from T_2-store-T_2 NMR experiments in bimodal pore systems.

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Diffusional pore coupling is an important issue in the NMR characterization of multimodal porous systems such as complex carbonates and shaley sandstones. Essentially, the pore size distribution deduced from conventional T_2 distributions may give wrong estimations of porosity partitioning, especially at high temperatures typical of oil reservoir at which wide unimodal instead of bimodal distributions may be observed. Recently, Montheillet et al.[1] proposed a two dimensional T_2-store-T_2 experiment to study proton exchanges in cement pastes. We applied this sequence to study and quantify the pore coupling in carbonates and clay-sand mixtures.

The T_2-store-T_2 experiment is an elegant method to demonstrate and quantify pore coupling. Depending on the exchange rate between two pore populations, off-diagonal peaks may appear in a T_2-T_2 correlation plot. Using an analytical solution, a parametric study indicates that the amplitude of the off-diagonal peaks is usually only a few percent of the largest on-diagonal peaks. Using our 2D Laplace inversion software, we show that the detection of small amplitude peaks is possible but their location may not be accurate. We show different examples (Fig. 1) of T_2-store-T_2 experiments. For each case, the existence of pore coupling is also verified qualitatively by observing the shift of the micro/macro porosity peaks in the T_2 distribution at different temperatures.

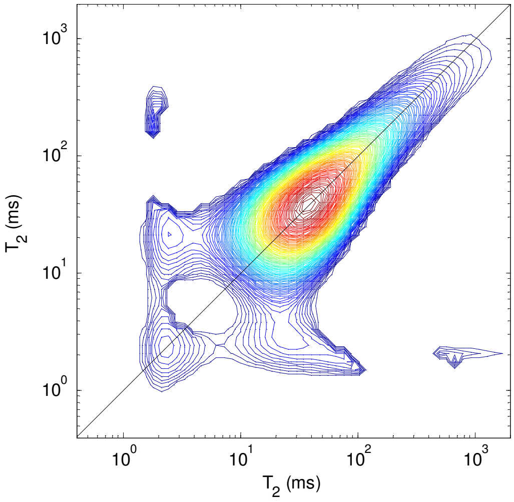

Fig. 1: Result of a T_2-store-T_2 experiment on a bimodal carbonate sample (Lavoux). Mercury porosimetry and MEB observations clearly indicate two pore populations, whereas the 1D T_2 distribution is wide and unimodal. The strong coupling occurring on that sample is expressed as a distribution of off-diagonal peaks. (Storage time 90 ms, Larmor frequency: 23.7 MHz).

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Method and Experimental Study of 2-D NMR Logging

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Abstract As the signal of reservoir fluids, such as oil, gas and water, always overlap in the T_2 distribution of nuclear magnetic resonance (NMR). It is difficult to identify fluid types effectively by 1-D NMR logging. Considering the characteristic of transverse relaxation (T_2), longitudinal relaxation (T_1), diffusion coefficient (D) synthetically, we can perform the measurement of two-dimension NMR (2D-NMR), which has provided the foundation for qualitative identifying and quantitative evaluation of the reservoir-fluids. Three methods of 2D-NMR logging were proposed and several forward models were designed accordingly. And 2D information of (T_2, D), (T_2, G) and (T_2, T_1) was acquired by measuring multiple CPMG pulse sequence with variable echo spacing (TE) and waiting times (TW) respectively. Then we had got the 2D proton density distribution through multi-exponential inversion method. At last, in order to prove the measuring and data processing methods, the experiments of 2D-NMR with some man-made rocks and natural core samples are performed. It had identified fluid types clearly, calculated fluid-saturation exactly, and detected the distribution of internal field gradients of core samples which contain paramagnetic minerals.

Keywords 2D-NMR logging, Transverse-Relaxation, Longitudinal-Relaxation, Diffusion-Coefficient, Gradient Fields

Methodology on Searching for Similarities between the NMR Relaxation Spectra and Reference Logs

P. Romero

Baker Hughes, division Baker Atlas

This paper presents a technique on searching for similarities between Nuclear Magnetic Resonance (NMR) logging spectra and reference logs or associated information. The fundamental approach for implementing this technique relies on understanding each of the bins, or discrete values, of the NMR spectra as individual logs or a time series (depth). These NMR bin logs can be easily set in relationship to additional logs, e.g. resistivity, saturation or gamma ray, without restricting their general applications.

The Pearson correlation and the entropy-based mutual information have been chosen as two basic tools for searching for log-log similarities. Figure 1 shows an averaged T2 distribution over a certain depth interval, and a color-coded degree of correlation with the resistivity log. When using the Pearson correlation approach, the p-value provides an additional method to validate the degree of correlation on a statistical basis.

Figure 1 shows an averaged T2 distribution for a certain depth interval and color-coded information regarding the degree of correlation of the T2 spectra with a resistivity log. Dark blue color can be interpreted as predominantly water, and dark red can be interpreted as hydrocarbon.

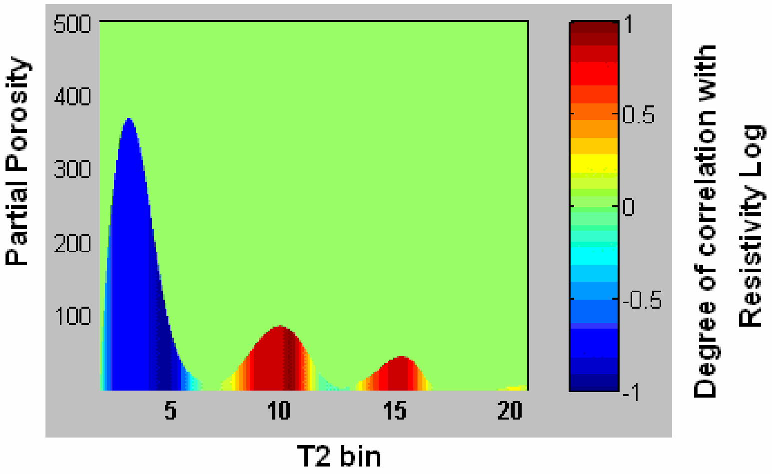

Fig. 1 T2 distribution and color-coded correlation with resistivity log

This method can be applied widely. The information it generates can contribute to reduce uncertainties in the formation-evaluation process.

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On the use of two dimensional inverse Laplace routines on NMR data

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Keywords. Inverse Laplace, relaxation, diffusion, porous media

When applied to NMR data arising from relaxation time and diffusion experiments, either in combination (two dimensional) or as single experiments, the use of Inverse Laplace routines has become a crucial tool in NMR data analysis.

After working with numerous rock core plugs at different saturation states over a period of five years we have concluded that it is impossible to draw good conclusions from the NMR data when applying well known algorithm which estimates continuous distributions of the inverse Laplace transform.

A typical problem with the routines currently in use, is the fundamental error that is produced when defining the grid as an input to the numerical routines. As the responses from any fluid confined a porous rock may locate peaks off from the grid points, the resulting distributions will be wrong. In particular we have found that the current routines fail to fit the estimates of the total NMR signal.

One may of course adjust the grid so that one achieves as good a fit as possible, but that relies on the brave assumption that any multimodal distribution may be fitted to that set of grid points. In practical life this is the exception not the rule, i.e. it is not possible to fit all peaks to the grid points available once having defined the grid. The underlying problem is that estimating an inverse Laplace transform with continuous distributions is an attempt at forcing too much information out of experimental data.

When using the ANAHESS algorithm, the situation is different. No grid is defined, and the numerical routine fits the NMR data to the peak values that yield the best fit. When comparing the residuals from the two routines we find the ANAHESS overwhelmingly superior.

A Fast Monte Carlo Sampler for NMR T2 Inversion

M. Prange

Schlumberger-Doll Research

The inversion of noisy NMR T2 echo data a T2 spectrum is widely recognized as an inherently non-unique process [1]. One approach to quantifying this uncertainty is to use Monte Carlo sampling. Measurement noise is well described by an uncorrelated normal distribution. When combined with the non-negativity constraint on T2 spectral values, this leads to spectral values following a non-negative normal distribution. There are published samplers for truncated normal distributions [2], of which non-negative normal samples are a subset, but I show that these converge very slowly for the highly ill-conditioned covariance matrices that are present in NMR T2 spectral inversion. The reason for this is that they are based on Gibbs' samplers that update the spectral estimate just one T2 component at a time. When all of the spectral elements are fixed but one, that one has little room for change without violating the noise constraints on the data. This means that each spectral sample can only be slightly different from the preceding sample, indicating a high degree of statistical correlation and thus slow convergence. I resolve this by simultaneously updating two neighboring spectral components at a time, allowing changes due to one spectral component to be offset by changes in its neighbor. Core to this improvement is a fast 2D sampler for non-negative normal distributions. I demonstrate that this improves convergence by more than two orders of magnitude. Such speedup allows routine Monte Carlo inversion of 1D NMR spectra, and opens the door for the inversion of 2D NMR spectra.

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Signal Optimization in Inhomogeneous Fields: Application of Optimal Control Theory to NMR Oil-Well Logging

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Nuclear Magnetic Resonance (NMR) techniques are especially useful in well logging to characterize hydrocarbon bearing geological formations surrounding a bore hole. The Carr-Purcell-Meiboom-Gill (CPMG) sequence forms a key element is all measurements that determine the relaxation and diffusion properties (see Ref. 1). Our ability to accurately perform these measurements, however, is severely limited by environmental constraints. The necessity of designing a magnetic resonance tool to be placed inside a drilled well leads to gross in-homogeneity of the applied static and RF fields. Being a resonance phenomenon, NMR requires the Larmor precession frequencies of nuclear spins in a static field to be close to the frequency of the applied RF field. Field in-homogeneity leads to a spatial variation of Larmor frequencies and the effective RF field strength a spin experiences. Thus, the obtainable signal is limited by the number of spins excited and refocused uniformly by the pulses in the CPMG sequence. We demonstrate the use of Optimal Control Theory (OCT) techniques to design complex amplitude and frequency modulated pulses that extend the effective bandwidth of uniform control to a range well beyond that achievable via conventional 'hard' pulse techniques. OCT techniques have previously been used in the design of NMR pulses, (see e.g. ref. 2), but this is the first time that it has been used to the study of Carr-Purcell dynamics in inhomogeneous fields. We find that these advanced techniques allow us to maximize the signal over a significantly wider dispersion of Larmor frequencies. Compared to standard hard pulses, the excitation/refocusing bandwidth for OCT pulses can be increased at least four-fold. The pulses also have the convenient property that they are phase-distortionless. They can therefore be directly substituted into any sequence to enhance performance without further need for modification, making the pulses appropriate for a wealth of applications beyond what we have considered in this study. Additionally, analysis of the asymptotic echo amplitude and phase created by directly substituting our pulses into the Carr-Purcell sequence demonstrates stability in the absence of T_2-relaxation and diffusion consistent with the Meiboom-Gill correction. This indicates that the CPMG sequence using directly substituted OCT pulses will significantly enhance the signal-to-noise ratio of diffusion and relaxation measurements in oil-well logging.

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Split-180^o Sequences

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In applications of NMR in inhomogeneous fields, sequences based on the Carr-Purcell-Meiboom-Gill (CPMG) sequence play a central role. The standard CPMG sequence consists of an initial 90^o excitation pulse, followed by a long string of 180^o refocusing pulses. This creates a series of echoes that decay with a characteristic relaxation time T_{2eff}.

Here we present a modified sequence, the so-called *Split-180^o* sequence that specifically takes advantage of grossly inhomogeneous fields. In its simplest implementation, the 180^o refocusing pulse of the CPMG sequence is split into two separate pulses. This sequence, which can be viewed as a modification of the CPMG sequence, simultaneously generates two types of signal that can be separately detected. One is a CPMG-like signal that decays with the expected relaxation time T_{2eff}. In addition, a second type of signal builds up and approaches a steady-state. The amplitude of this dynamic equilibrium depends on the ratio of the longitudinal to the transverse relaxation times, T_1/T_2.

We present experimental results and a new theory that describes both signals in a unified manner.

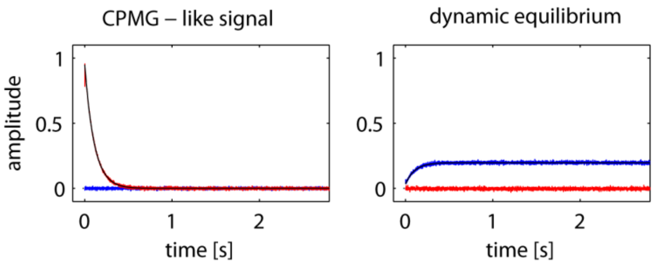

Fig. 1: Experimental results of the split-180^o sequence on a sample of doped water with a relaxation time $T_1 = T_2$ of 100 ms. The left panel shows the amplitudes of the CPMG-like signal that decay towards zero with T_2, whereas the right panel displays the amplitudes of the dynamic equilibrium signal that rise towards a constant amplitude.

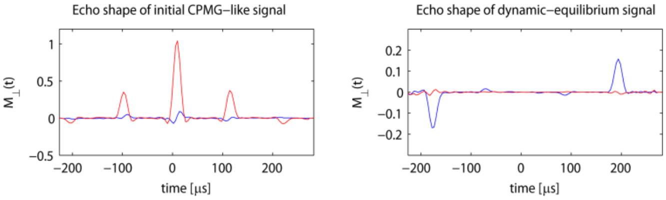

Fig. 2. Echo shape of the CPMG-like signal (left) and the dynamic equilibrium signal (right). The CPMG-like and the dynamic equilibrium signals form out of phase to each other.

Measurements of diffusion, T_1 and T_2 in one-shot by MMME

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In the presence of a constant gradient field, a sequence of *n* hard RF pulses will allow multiple coherence pathways (*q*) to produce multiple signals. This class of sequences is called multiple modulation multiple echoes (MMME)[1-4]. Different *q* creates different spatial phase modulation and yields echo signal at different time. Consequently, in one scan of the sequence, different modulations can be acquired. By setting the time period appropriately, the 4-pulse MMME sequence can give well separated 13 echoes for acquisition. The magnetization of each echo coherence pathway (i.e. each echo *q*) is a product of three factors: the RF pulses (α), the diffusion (*D*), and the relaxations (T_1, T_2). It can be written as:

$$M_q = M_0 \cdot f_q(\alpha) \cdot \exp(-b_q \cdot D) \cdot \exp\left(-\frac{c_q^1}{T_1} - \frac{c_q^2}{T_2} \right),$$

where M_0 is the initial total magnetization, the coherence pathway *q*. The symbols b_q, c_q^1 c_q^2 are sequence dependent diffusion, T_1, and T_2 weighting factors, respectively. In practice, for two measurements with same RF flip angles, but different time delays, the ratio of the corresponding echo magnitudes will eliminate $f_q(\alpha)$. The amplitude ratios S_1/S_2 and weighting factors of the corresponding 13 echoes give sufficient data to uniquely determine *D*, T_1 and T_2 simultaneously.

Different echo spacing and gradient strength will result in different diffusion and relaxation weightings for each coherence pathway, thus offer a mechanism for optimization. For the sequence with the optimized parameters, synthetic data were generated by giving a random error of 3% on each echo signal, and the standard deviation of T_1, T_2 and *D* were calculated for different T_1, T_2 in the range of 20 - 2000 ms ($T_1 \geq T_2$) with a constant D value. It can be seen, that using giving sequences, the error propagators in *D*, T_1 and T_2 are controlled within 10% (Fig.1). Experimentally, the MMME obtained values showed a good agreement with those from standard Pulsed Filed Gradient (PFG), Inversion Recovery (IR), and CPMG measurements.

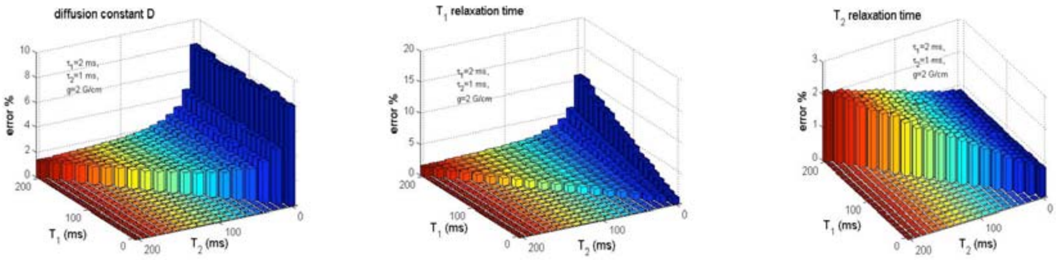

Fig. 1: Calculated standard deviation of D, T_1, T_2 for optimized MMME sequences with a random error of 3% on each echo signal.

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Double-PFG Diffusion-Diffraction in Ellipsoidal Pores

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Repeated application of diffusion gradient pulse pairs [1] in a pulsed field gradient (PFG) experiment provides important insights into pore microstructure. For example, the dimensions and eccentricity of yeast cells were measured from the fourth order term of the double-PFG signal attenuation when the mixing time between the two encoding blocks is long [2]. In this abstract, we propose an alternative double-PFG technique to address the same problem, which exploits the diffusion-diffraction phenomenon [3] in double-PFG experiments [4]. In our approach, all diffusion gradients in a single acquisition are applied along the same direction with a mixing time of 0. The experiment is subsequently repeated with diffusion gradients applied along different directions.

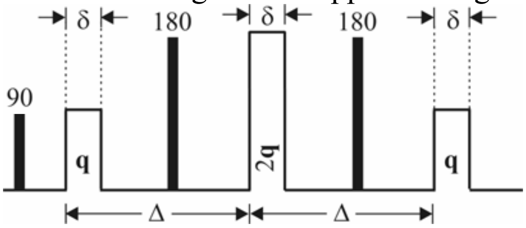

Fig. 1: The double-PFG pulse sequence considered in this work. The duration of the diffusion gradients (δ) are assumed to be very short. $q=\gamma\delta G/2\pi$, where γ is the gyromagnetic ratio and G is the gradient strength. The separation between subsequent pulses (Δ) is assumed to be long enough so that a spin can probe the largest dimension within the pore.

As demonstrated in [4], the expected signal for this pulse sequence is given by $\tilde{\rho}(q)^2\,\tilde{\rho}(2q)^*$, where $\tilde{\rho}(q)$ is the Fourier transform of the pore shape function. This expression for the NMR signal attenuation leads to two interesting observations: (i) the first signal minimum occurs at exactly half the q-value necessary to observe nonmonotonicity in a single-PFG experiment; (ii) the diffraction minima are replaced by zero-crossings making the diffraction pattern robust to the heterogeneity of the specimen. We calculated the NMR signal attenuation from ellipsoidal pores with different eccentricities using the expressions in [5].

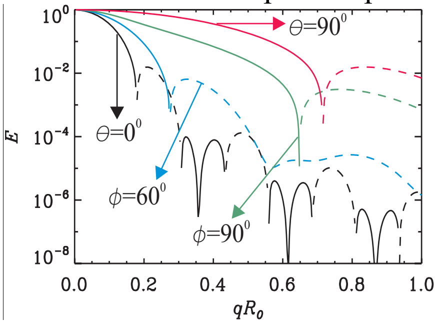

Fig. 2: The continuous and the dashed portions of each curve correspond to the positive and negative signal values, respectively. Black and red curves are computed for coherently oriented, axially symmetric ellipsoids whose ratio of major to minor axes was 4. The black curve is expected when the gradients are applied along the major axis, whereas the red curve is expected when the gradients are in the transverse plane. The blue curve shows the signal from ellipsoids whose axes are uniformly distributed over a spherical cap between the polar angles $\theta=0^0$ and $\theta=60^0$. The green curve is predicted for isotropically distributed pores.

The proposed method makes it possible to observe diffusion-diffraction phenomenon in anisotropic pores even when the pore orientations are randomly distributed. The first zero-crossings of the diffraction patterns with gradients applied along different directions can be used to quantify the compartment size as well as the pore shape anisotropy using double-PFG acquisitions with 0 mixing times, hence mitigating the effect of relaxation-related signal loss.

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This research was supported by the intramural research program of NICHD.

Accurate RTOP Estimation from PFG-NMR Signal

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The return to the origin probability (RTOP) for diffusing molecules is a valuable indicator of porous media microstructure [1-2]. For example, in isolated pores with non-relaxing walls, the pore volume is related to the RTOP at long diffusion times. Similarly, in disordered media, the temporal scaling of the RTOP is necessary in the estimation of the fractal dimension of the medium [3]. However, the RTOP is related to the pulsed field gradient (PFG) NMR signal via an integration over the entire q-space. The unavailibility of data at large wavevectors is a serious problem particularly in restricted domains where the NMR signal does not attenuate significantly even at relatively large wavenumbers.

In principle, the extrapolation of the signal values can be performed by model fitting to data. However, very different signal profiles are possible depending on the particular specimen under examination whose structure is not known *a priori*. Another alternative is the cumulant expansion, which may fail to converge to the true signal attenuation. Fig. 1a shows the failure of both the cumulant expansion and sometimes used biexponential fitting in describing the theoretical signal attenuation from rectangular pores at long diffusion times.

In this work, we propose to represent the PFG-NMR signal in terms of a complete set of Hermite functions. The basis possesses many interesting properties relevant to q-space NMR, such as the ability to represent both the signal and its Fourier transform. Unlike the previously employed methods, this approach is linear and capable of reproducing complicated signal profiles, e.g., those exhibiting diffraction peaks. The estimation of the coefficients is fast and accurate while the representation lends itself to a direct reconstruction of ensemble average propagators as well as calculation of useful descriptors of it, such as the RTOP and its moments.

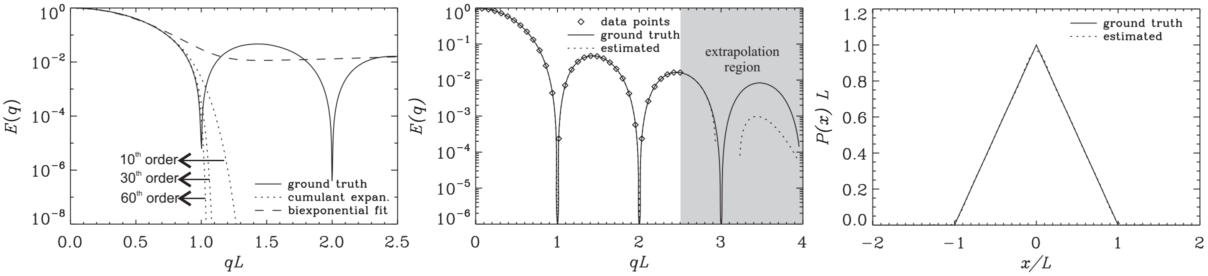

Fig. 2: PFG-NMR signal attenuation curves from rectangular pores at long diffusion times. (a) Cumulant expansion of and biexponential fit to simulated data. (b) The performance of the proposed approach with the same data. (c) Propagator reconstructed from the basis functions whose value at x=0 is the RTOP.

We performed simulations to assess the performance of the RTOP estimations for one-, two- and three-dimensional, isotropic, restricted media as well as mono- and bi-exponential decays and even the presence of flow was considered. RTOP values in 1-, 2- and 3- dimensions all yielded very accurate results (<6% error in restricted geometries, <1% in others). The proposed approach is expected to improve the accuracy of RTOP estimates and parameters deduced from it.

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This research was supported by the intramural research program of NICHD.

Measurement and simulation of the non-local dispersion tensor in porous media

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Dispersion describes the phenomenon whereby particles on the same streamline separate during flow. The physics of dispersion is governed by stochastic processes arising from the interplay between advective velocity gradients, molecular diffusion and boundary layer effects[1]. The dispersion tensor, $\mathbf{D}^*$, is a local measurement in the sense that it does not depend on positional relationships and is measured as time asymptotes[2]. For situations where the length- and time-scales on which transport occurs are not much larger than the scale of the fluctuations in the velocity field, a non-local description is required[3]. The tensor is written as

$$. \ \mathbf{D}^*_{\mathrm{NL}}\left(\mathbf{R},\tau\right)=\left\langle \mathbf{u}\left(\mathbf{r},0\right)\overline{P_{\mathbf{r}}}\left(\mathbf{R},\tau\right)\mathbf{u}\left(\mathbf{r}+\mathbf{R},\tau\right)\right\rangle$$

Pulsed Gradient Spin Echo (PGSE)-NMR provides a wealth of information about the velocity correlations in porous media. Presented here is a set of NMR pulse sequences and a superposition designed to extract the velocity correlations necessary to calculate the dispersion as a function of displacement and hence the non-local dispersion. The experimental method will be tested against the calculable non-local dispersion in a Couette cell[4]. Further experiments are performed on porous media over a range of Peclet number and further tensors will be discussed.

The Lattice-Boltzmann algorithm has been shown to successfully predict the flow field in porous media[5], and has been used to model the flow field through our model porous medium. This flow field is used to simulate a large ensemble of virtual tracer particles, from which numerical estimates for both the local and non-local dispersion can be determined. Our implementation of this approach is presented here along with a comparison between the experimental and computational results.

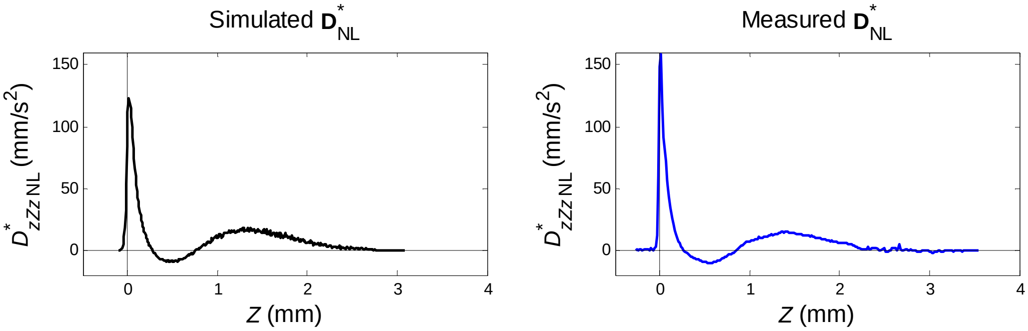

Fig. 1: The non-local dispersion of flow through a beadpack, Pe = 2000, V_t = 8mm/s, $\tau = \tau_v$, d_{bead} = .5mm.

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Restricted self-diffusion in pure water measured by NMR

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The current thinking, influenced greatly by molecular modeling simulations[1], is that on a very short pico-second time scale, water is more like a "gel" consisting of a single, huge hydrogen-bonded cluster. Rotations and other thermal motions cause individual hydrogen bonds to break and re-form in new configurations, inducing ever-changing local discontinuities whose extent and influence depends on the temperature and pressure. Over very small volumes, localized $(H_2O)_n$ polymeric clusters may have a fleeting existence, and many theoretical calculations have been made showing that some combinations are stable enough to prolong their lifetimes. But it is considered that they does not remain intact long enough to be observed in ordinary bulk water at normal pressures.

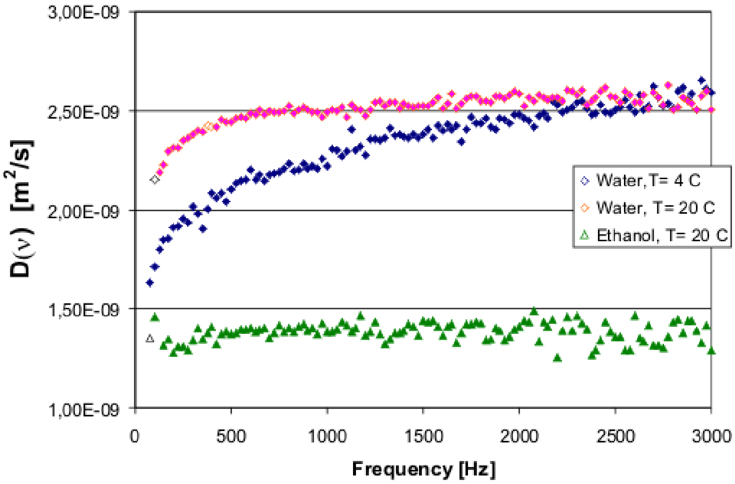

Fig. 1: Molecular velocity autocorrelation spectra of pure water at different temperatures as measured by modulated gradient spin echo method. The constant spectrum value of non polar ethanol emphasizes the role of hydrogen bonding at the diffusion of water molecules

Thus, the measurements of the pure water self-diffusion by a new modulated gradient spin echo method[2] came as surprise giving the frequency dependence of the water velocity autocorrelation spectrum. The spectrum decrease in the low frequency range with almost linear dependence on $D(\nu)$ versus $1/\sqrt{\nu}$ plot resembles the restricted molecular motion. Constant spectrum value of nonpolar ethanol in the low frequency range, as shown in Fig. 1., gives an indication about the water diffusion constrained by the hydrogen bond interaction.

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Design of anisotropic fiber phantoms for the validation of diffusion weighted magnetic resonance imaging

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A gold standard for the validation of diffusion weighted magnetic resonance imaging (DW-MRI) is essential for clinical purposes but still not available. Anisotropic diffusion fiber phantoms (Fig. 1) have been proposed recently for this purpose [1]. A crucial question is how the different material properties and size of the fiber phantoms influence the outcome of the DW-MRI experiment.

Three potential fiber materials for constructing fiber phantom were studied: Dyneema (∅ 16 μm), Nylon (∅ 64 μm) and glass fiber (∅ 7 μm). Besides the fractional ansitropy (FA), the T_2-relaxation time and proton density of the fiber phantoms were evaluated since they define the signal-to-noise ratio (SNR).

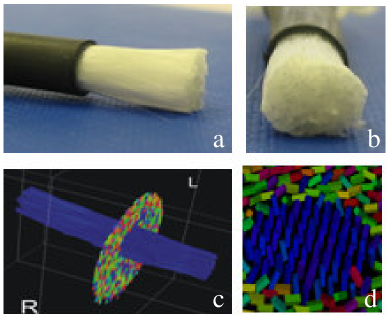

Fig. 1: Fiber phantom: longitudinal view (a) ,transversal view (b), fiber tracking results (c), color-encoded FA-map (d).

The fiber phantoms can be considered as two dimensional porous media with a matrix consisting of parallel randomly packed cylinders and the theory for diffusion [2] and R_2-relaxation [3] in porous media was used as a model. In addition, the diffusion inside the fiber phantoms and the effect of surface relaxation has been simulated using Monte Carlo simulations of random walk and verified against experimental FA and R_2-values. The fiber density and fiber diameter turned out to be the major factors determining the FA (Fig. 2), while for the R_2, the surface relaxation (Fig. 3) and the magnetic susceptibility of the fiber (Fig. 4) are the most determinant. The most appropriate fiber phantoms for the quantitative validation of DW-MRI are densely packed fiber phantoms made from a hydrophobic material with a magnetic susceptibility close to water.

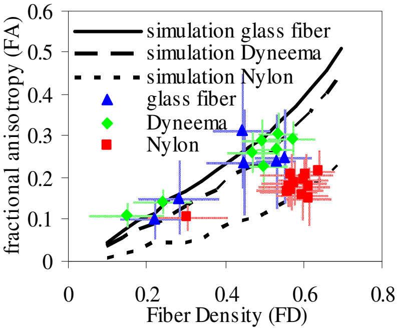

Fig. 2: Comparison between the measured and simulated FA-values. FA increases with increasing fiber density and decreasing diameter. Glass fiber and Dyneema have the highest FA.

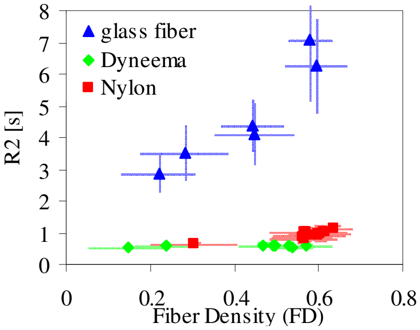

Fig. 3: R_2 rates depend differently on the fiber density due to the different fiber surface relaxivities. Dyneema has the lowest surface relaxation (0.13 μm/s).

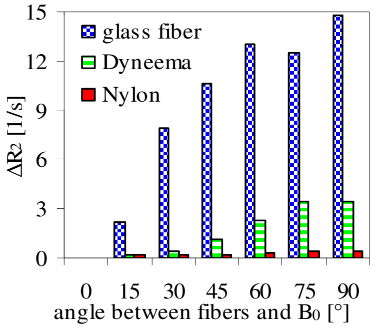

Fig. 4: The increase in R_2 when changing the angle between the fibers and B_0 depends on the susceptibility of each fiber materials. Nylon has the closest susceptibility to water.

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A numerical method to optimize presaturation sequences on multiexponential samples

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We have developed a mathematical model to simulate the effects of pulse sequences on composite samples and coded it in Matlab. The object-oriented code accommodates pulse sequences and samples of any complexity, including ones with any distribution of relaxation rates and offsets. Of equal importance is the fact that the most common instrumental artifacts (B_0 and B_1 inhomogeneity) can be easily taken into account. The package permits to simulate the magnetization of a composite sample during the whole sequence by using Bloch equations to track the magnetization of each sample component. The software allows one to obtain three quality factors related to: the highest residual magnetization among all components (Q_1); the square mean of all the residual magnetization components (Q_2); the modulus of the total magnetization vector of the sample (Q_3). Low values of Q_i (i=1,2,3) indicate good zeroings of the sample residual magnetization. In particular, a low value of Q_1 indicates good zeroing of all the sample residual magnetization components.

This approach has been applied to the problem of *fast and efficient presaturation* by a suitable *Sample Magnetization Suppression* pulse sequence (SMS) in the presence of a wide spread of offsets, relaxation rates, and magnetic field imperfections. This led us to the *Logarithmically-distributed A-Periodic Saturation Recovery* sequence (LAPSR) which comes as close as possible to suppressing the *absolute* magnetization of *all* sample components and is, in this respect, much better than the classical sequences Saturation Recovery (SR) and A-Periodic Saturation Recovery (APSR). LAPSR is characterized by the following pulse sequence:

$$\boldsymbol{P(\alpha) - D - P(\alpha) - D\cdot q - P(\alpha) - D\cdot q^{2} - \ldots - P(\alpha) - D\cdot q^{n-2} - P(\alpha) - D\cdot q^{n-1} - P(\alpha)} - \tau - 90^\circ,$$

where D is the delay between the first two presaturating pulses and α the nutation angle of the magnetization vector for each pulse. We notice that delays between presaturating pulses decrease logarithmically by a factor $q<1$ to reach the value $D\cdot q^{n-1}$ between the last two pulses of the presaturating sequence. The code was also used both to optimize LAPSR parameters, i.e. the delay D, the angle α, the number n of presaturating pulses, the q-value, and to show the effects of field inhomogeneities.

The performance of LAPSR has been verified on a composite large-volume phantom.

Study of water permeability and dynamics in micelle, vesicle and lipid bilayer systems using Dynamic Nuclear Polarization

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In nature water dynamics and content play a key role in the characteristics and functions of micelle-vesicle and lipid bilayer systems. Experimentally these are difficult parameters to access because the internal or bound water is difficult to discern from bulk water by conventional spectroscopic methods. We use dynamic nuclear polarization (DNP) to amplify the ^{1}H NMR signal via electron spins that are in dynamic dipolar interaction with the ^{1}H nuclei of water. Thus, DNP detects amplified ^{1}H NMR signal through polarization transfer from the spin label's unpaired electron giving us information about local water dynamics, while electron spin resonance (ESR) directly detects the spin label's signature and reports on the rotational diffusion of the spin labeled molecular segment. Here we show how ^{1}H DNP and ESR can give complimentary information on water permeability, dynamics and chain mobility in vesicle structures formed by Fatty acids (oleate) or cationic and anionic lipids respectively. Lipid bilayer model systems with and without membrane protein Proteorhodopsin incorporated, or with DNA spacers have also been investigated, by means spin labeles at head (16-PC Tempo) and tail (16-PC Doxyl) groups.

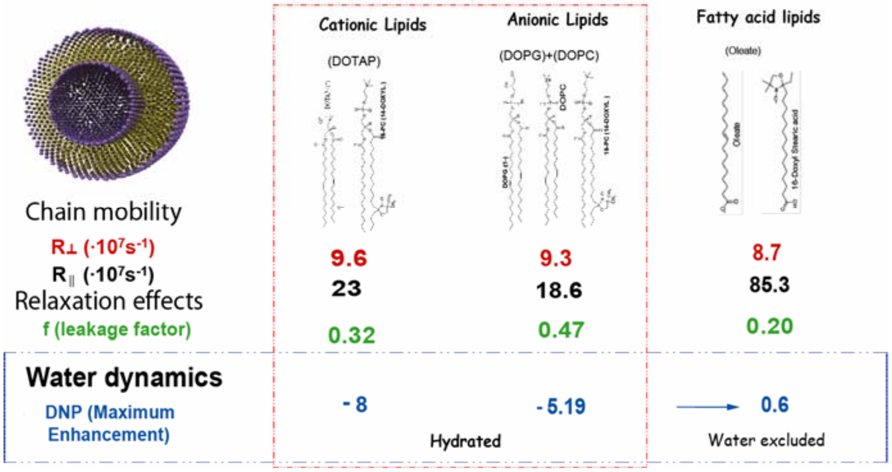

Fig 1. The DNP (maximum enhancement) values show us how hydrated cationic and anionic vesicle systems are in comparison with oleate vesicles. The rotational correlation times obtained by fitting the Cw X-band ESR spectra give us an idea of the mobility of the chain segment in the vesicles.

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Enhanced Overhauser contrast in low field images of a gelling process

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Magnetic Resonance Imaging (MRI) is a useful tool in material science applications. By looking at the image profiles it is possible to assess aspects of the structure, the underlying mechanisms of transport and chemical kinetics of processes. In MRI the signal amplitude detected from the magnetized sample is known to be proportional to the polarizing magnetic field. However, the MR signal can be enhanced by methods other than by increasing the field. One example is dynamic nuclear polarization (DNP), in particular the electronic Overhauser effect, whereby the polarization of a pool of unpaired electrons (a nontoxic free radical dissolved in water) is transferred, via saturation of the electronic transition, to the water molecules in the sample. It turns out that, in addition to the improved signal-to-noise ratio, for systems exhibiting changes in water mobility there is a remarkable enhancement in the contrast compared to that obtained by conventional T_2-weighted imaging [1]. This methodology offers accessibility to potential new effects [2] while using magnet design and cost much more affordable.

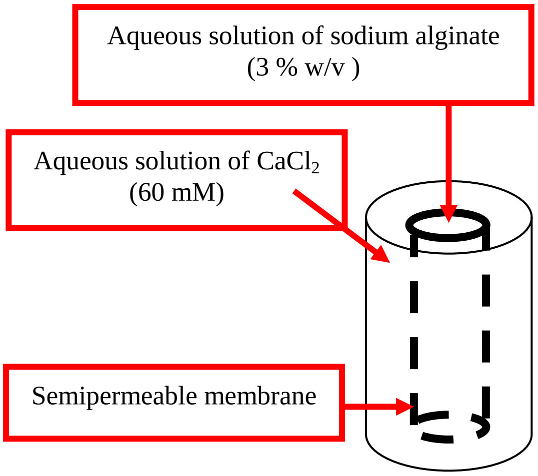

Fig.1 Sketch of the experiment: A cylindrical vial containing a semi-permeable (permeable only to small ions) dialysis membrane. The membrane contains a dilute solution of sodium alginate that is immersed into the vial containing $CaCl_2$. When the $CaCl_2$ crossed the membrane it reacts with the alginate forming the gel.

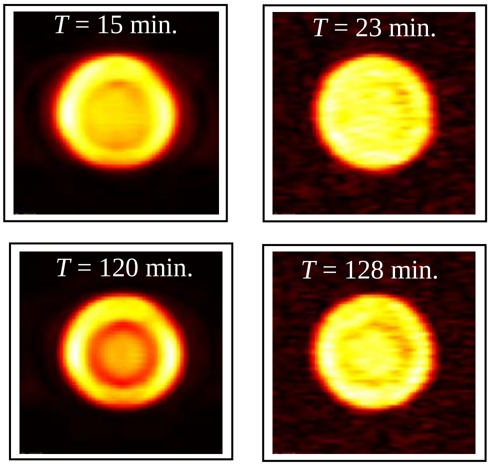

Fig.2 Gelling process of a sodium alginate solution in the presence of calcium ions crossing a semi-permeable membrane. Left column shows images obtained via PEDRI for two different gelling periods. The right column shows similar intervals where the contrast originates only from T2- weighting.

Although gels exhibit solid-like characteristics on a macroscopic level, microscopically they behave in a liquid-like fashion suitable for MRI investigation. Indeed, a considerable variation in water mobility is expected during the formation of gel systems. In order to demonstrate the enhanced mobility-contrast sensitivity generated via the Overhauser effect, we compare images of the formation process of alginate hydrogels obtained under the same experimental conditions by a technique named Proton-Electron Double-Resonance Imaging (PEDRI) [3] and by conventional T_2-weighted imaging.

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MRI with Hyperpolarized ^{3}He and ^{129}Xe at Very-Low-Field

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Studies employing hyperpolarized spin samples offer the possibility of high-sensitivity NMR and MRI at very low fields. Benefits include significantly reduced effects from susceptibility-induced background field gradients, often resulting in significantly longer T_2^*; and a greater skin depth that allows imaging inside conductors [1]. Without hyperpolarized samples, studies have been performed in the earth's field, partly for some of the above reasons [2,3]. For lossy samples, such as human subjects, additional benefits can be recognized. We have designed and built an open-access, very-low-field human MRI system that allows the study of pulmonary function with subjects in a variety of postures, an important advance in lung physiology. Despite the lower B_0 of our system, certain measurements that rely on accurate knowledge of B_1 homogeneity and RF flip-angle uniformity are simplified by operation at very-low-field.

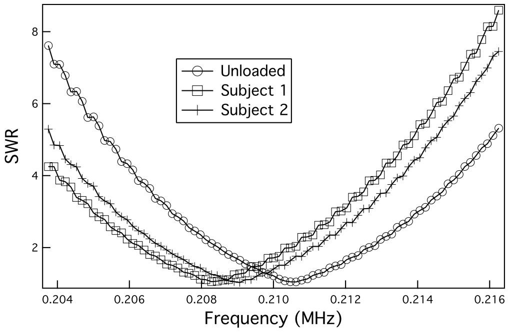

Fig 1: Measured SWR as a function of frequency for our human chest coil built for ^{3}He imaging at 210 kHz, when unloaded, and loaded by two different human subjects. The coil resonance shifts slightly, but coil *Q* is unaffected by subject loading.

T_2^* Contribution	B_0 = 1.5 T	B_0 = 6.5 mT
T_2 (s)	10	10
$T_{2,\text{ inhomogeneity}}$ (s)	0.143	0.016
$T_{2,\text{ susceptibility}}$ (s)	0.0046	1.10
$T_{2,\text{ diffusion}}$ (s)	0.031	1672
$T_{2,\text{ gradients}}$ (s)	0.512	3.6
T_2^* (ms)	3.8	15.6

Table 1: A comparison of T_2^* contributions at 1.5 T and 6.5 mT, along with the typical total value of T_2^*. A value of T_2 = 10 s is used in both cases [4], while $T_{2,\text{inh}} \sim 0.143$ s is used for 1.5 T [5]. All other terms are calculated from known values. ^{3}He T_2^* is based on our measured $B_0 \approxeq 0.4$ G, and 0.1 G for a 1.5 T scanner [6].

Operation below the "sample-noise dominance" regime means that our RF coil loads negligibly and reproducibly, regardless of subject. Coil *Q* is unaffected (Fig. 1). Therefore, the excitation flip-angle can be calibrated in advance, rather than being incorporated into every functional human lung study, as is done at high fields. Additionally, our calculations show that T_2^* contributions from susceptibility differences and diffusion through inhomogeneous background fields are negligible, and these effects combine to produce a T_2^* significantly longer than measured at high field (Table 1). As hyperpolarized liquid species gain popularity, similar benefits could be realized in many biomedical and materials studies.

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Accumulation of NMR Data in Polar Coordinates and Numerical Methods to minimize Systematic Errors

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Abstract:

In this work we present new instrumental concepts and new NMR methods based on the acquisition and the accumulation of the signal magnitude. The method has been developed to overcome field stability limits and allow the acquisition of Hahn echo decays in Fast Field Cycling Technique

Nevertheless the accumulation of signal magnitudes of NMR data in low signal-to-noise ratio (SNR) regimes produces signal-dependent noise bias that reduces the accuracy of the measurements. This is particularly important for T1 and T2 measurements when the relaxation curve are fitted by a multi-exponential acquisition from polar coordinates. In fact the white noise, with a Gaussian distribution, that affect the NMR signal, become a Rician noise, characterized from the Rayleight distribution, on the accumulated signal magnitudes resulting in a systematic error.

We have developed the correction scheme on a reconfigurable digital hardware architecture, to apply the factor directly over the data-flow on our acquisition channel

Further developments are focused on the improved hardware implementation of numerical methods used to calculate the correction factor. We have also proposed a different technique in order to better evaluate SNR dependencies and extract the real signal intensity from noisy magnitude MNR signals. This alternative technique presumes the possibility of measuring the power of the noisy signals.

Several numerical approaches have been proposed in literature to de-noising NMR signals including a non-linear and wavelet transform. These methods are suitable to be use in a post-processing data evaluation. Used in conjunction with our hardware correction technique, become a complete tool to compensate and/or remove noise from digitalized NMR signals.

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Delayed Focus-Pulses in Projection Reconstruction

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With the advent of newer and more robust MRI techniques, Projection Reconstruction (PR) has become a somewhat retired method due to the probe dead time plaguing the gross structure of its images. In fact, virtually all FID experiments suffer from the same dead time, which effectively ignores the first few microseconds of any signal, the first few crucial k-space data points likewise in MRI. Dead time aside, the ability to rapidly sample an FID signal on a polar k-space raster while monitoring its progress makes Projection Reconstruction in principle a very worthy contender for imaging short T2* species, including porous media and fluid flow measurements. In this talk, the Delayed-Focus Pulse [1] (DFP) will be introduced as a potential cure to the dead time plague. The DFP is so-called due to its phase-refocusing property that causes the signal to achieve phase coherence at a time $\mathbf{t_f}$ after the initial pulse based entirely on the customizable shape of the pulse itself. Combining the concepts of PR and the DFP, a new imaging sequence will be discussed and compared with other well-practiced techniques such as the Double-Half k, RARE and SPRITE. Understanding where this new method stands will be a step forward in hopes that its uniqueness has a place in materials MRI.

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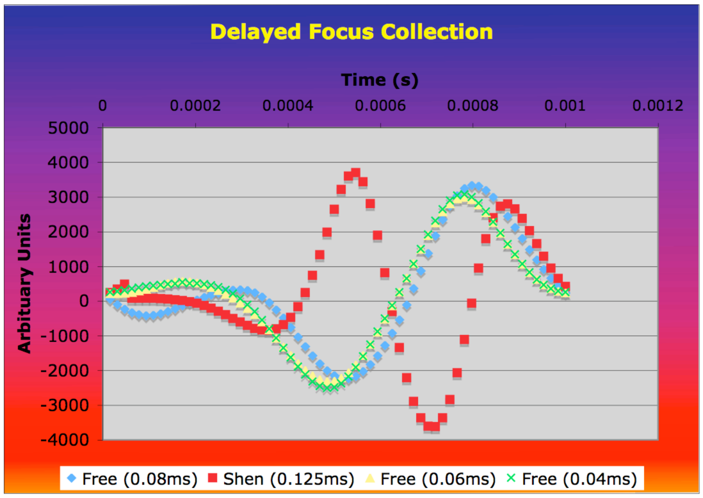

Fig: A collection of four Delayed-Focus Pulses whose delay times t_f are listed in the legend below.

Optimal *k*-space Sampling for Single Point Imaging of Transient Systems

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Magnetic Resonance Imaging has been used to visualise moisture absorption from humidified air, and subsequent diffusion of this absorbed water, in initially dry samples of food wafer. Due to the high porosity of the wafer (typically 80 – 90 %) and the typically low moisture content (of the order of 2-7 wt %), this is particularly challenging. The wafer also exhibits very short spin-spin relaxation constants, T_2^* (typically of the order of 50 μs) and T_2. Consequently conventional frequency encode techniques are precluded due to the unfavourable signal relaxation properties. Thus Single Point Imaging (SPI) [1; 2] is the main MRI technique used in the current study.

To overcome the main drawback of SPI, its relatively long acquisition time, a novel approach or trajectory for sampling ***k***-space is presented (the relatively long T_1 of the absorbed moisture excludes the use of SPRITE [3]). The sequence is optimised with respect to the achievable Signal-to-Noise ratio (*SNR*) over a given time interval via selective sparse ***k***-space sampling, the trajectory of which is dictated by prior knowledge of the overall object shape. Further modest improvements in image quality are also shown via the use of complete sampling of ***k***-space at the start or end of the series of imaging experiments (when imaging time is not limited by system dynamics), followed by subsequent use of this data for un-sampled ***k***-space points for intermediate images, as opposed to zero filling. This technique was successfully applied to follow the moisture absorption process by the wafer. Good image reproduction was achieved with significant under-sampling of ***k***-space. Error is shown to be significantly reduced relative to alternative sampling trajectories.

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A new theoretical insight on time-dependent diffusion coefficient

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In NMR, measuring the time-dependent diffusion coefficient $D(t)$ is an efficient tool to probe the geometry of porous media[1,2,3]. Although the diffusive motion is well understood in single-scale domains (slab, cylinder, and sphere)[4], many issues remain unclear for multi-scale porous structures like sedimentary rocks, cements, or biological tissues. To get a better theoretical insight onto restricted diffusion in multi-scale geometries, we study the spin-echo signal attenuation due to diffusion in circular and spherical layers, $\{x \in \mathbf{R}^d : L-l<|x|<L\}$, presenting two geometrical lengths, the radius L and the thickness l. Since the Laplace operator eigenbasis is known explicitly, many analytical results can be derived, in particular, the closed form for the time-dependent diffusion coefficient,

$$D(t)/D = \sum_{k=0}^{\infty} \lambda_{1k} B^2_{00,1k}\, w(D\, t\, \lambda_{1k}/L^2),$$

where D is the free diffusion coefficient, λ_{nk} the Laplace operator eigenvalues (here, only λ_{nk} with n=1 are involved), $\lambda_{1k}B^2_{00,1k}$ the explicit weighting coefficients[5]. The function $w(p)$ is determined by the temporal profile (or waveform) of the applied magnetic field gradient, e.g.,

$$w(p) = (1/p^2 - (\exp(-p) - 4\exp(-p/2) + 3)/p^3)/12$$

for the simple bipolar gradient (two rectangular pulses of duration $\delta = t/2$). For thin layers ($l << L$), a perturbative analysis gives surprisingly accurate results, e.g. $\lambda_{10} \approx 1$ and $\lambda_{1k} \approx \pi^2 k^2 (L/l)^2$ for circular layers. The "gap" between λ_{10} and λ_{11} is bigger for larger separation between two geometrical lengths L and l. A new, intermediate diffusion regime emerges for $l << (2Dt)^{1/2} << L$, when the echo time t is long enough for particles to travel between two boundaries, but still insufficient for exploring the whole domain. This diffusion time t appears as an experimental "yardstick" for probing geometrical lengths of the confinement. This intermediate regime resembles the tortuosity regime in porous media.

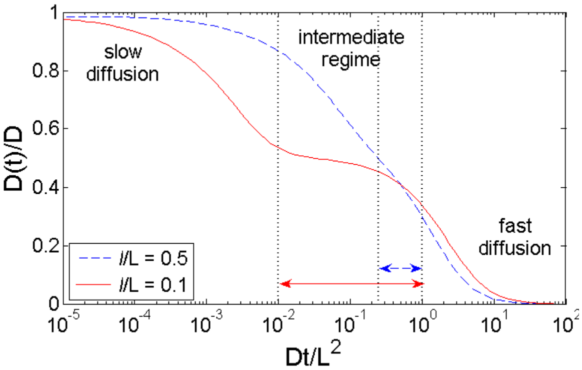

Fig. 1: Time-dependent diffusion coefficient $D(t)$ for thick (l/L = 0.5, dashed blue line) and thin (l/L=0.1, solid red line) circular layers. For thick layer, the scale window $0.25 << Dt/L^2 << 1$ (shown by vertical dotted lines) is too narrow, so that a mere transition between slow and fast diffusion is observed, as for the disk. For thin layer, the scale window $0.01 << Dt/L^2 << 1$ is large enough to reveal the new intermediate regime. At this time and length scales, restricted diffusion in a two-dimensional thin layer is effectively one-dimensional so that the apparent diffusion coefficient is reduced by factor 2, a kind of "tortuosity" of the thin layer.

In conclusion, we considered restricted diffusion in model two-scale geometries. In a single mathematical frame, we observed the transition from the slow diffusion to a new intermediate regime (analogous to the tortuosity regime in porous media), and then to the fast diffusion. These features should appear and be relevant for natural multi-scale structures.

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Quantitative NMR microscopy of iron transport in methanogenic aggregates

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Up-flow Anaerobic Sludge Bed (UASB) reactors are the most widely applied type of anaerobic waste water treatment reactors. The actual purification process takes place in methanogenic granular sludge that consist of rigid, well settling microbial aggregates that developed by the mutual attachment of bacterial cells in the absence of a carrier material. Heavy metal transport into these inhomogeneous, spherical biofilms is an important process both from the point of view of toxicity and bioavailability. Detailed experimental data on metal transport and biosorption within biofilm matrices is lacking due to the absence of adequate, non-invasive analytical tools, hindering refined modelling of these complex processes.

In this study 3D spatially resolved concentration mapping of iron as an environmental relevant, paramagnetic model metal is aimed for under strict requirements for spatial and temporal resolution. Although 3D T_1 mapping would be the most direct method, this approach does not fulfil these requirements. Mohoric *et al.* demonstrated the application of centred-out 3D RARE imaging to follow the highly dynamic process of cooking of a single rice kernel in a spatially and temporal well resolved manner (1). This technique was combined with the approach demonstrated by Nestle *et al.* to use image contrast to map metal concentration in alginate gels (2). Due to the short effective echo-time contrast is based on changes in T_1 as a function of metal concentration. Recently Graf von der Schulenburg *et al.* presented a less sensitive 2D approach using T_2 contrast to map cobalt concentrations in a model biofilm reactor (3).

The reaction-diffusion process of iron in two types of methanogenic granules from different UASB reactors was investigated. The inner structure of the different granule types revealed by 3D T_2 maps varied from a homogeneous matrix to a heterogeneous structure with voids and cracks. Detailed analysis of the 3D RARE datasets resulted in quantitative concentration profiles of iron inside the granules with a radial resolution of 200 µm and a time resolution of 11 minutes. Although iron transport into the granules is facilitated by presence of channels, the actual iron penetration into the matrix is mainly determined by the overall water content and diffusivity of the matrix.

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Asphaltene aggregation in crude oil studied by low field relaxation and diffusion measurements

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We used low-field NMR bulk relaxation and diffusion experiments to study aggregation properties of asphaltenes in crude oils. Asphaltenes are of particular interest in the oil industry, where their precipitation may clog up permeable pores and pipelines, causing huge losses at various production stages. Though many methods exist to study asphaltene properties, NMR has the potential to measure the asphaltenes in situ, downhole in their native environment, at the earliest stages of oil exploration.

We studied three sets of samples with varying asphaltene concentration at temperatures ranging from 45ºC to 92ºC and at Larmor frequencies of 1.7 MHz and 5 MHz. Asphaltene was first removed from the crude oil by heptane precipitation and then mixed back in different proportions, resulting in concentration range from 0% to 11%. Increasing asphaltene contents enhanced the relaxation, Fig.1(a), while leaving diffusion properties largely unchanged. T2 relaxation was affected more strongly than T1, consistent with the presence of large asphaltene clusters and resulting slowed correlation times. We found that only maltene (deasphalted crude) protons were observed, as asphaltene relaxed faster than our detection window. All the extra relaxation seen in Fig. 1(a) comes from maltene interactions with asphaltene clusters. Asphaltene, therefore, acts as a contrast agent with respect to the solvent maltene, and its effects are related to its aggregation state.

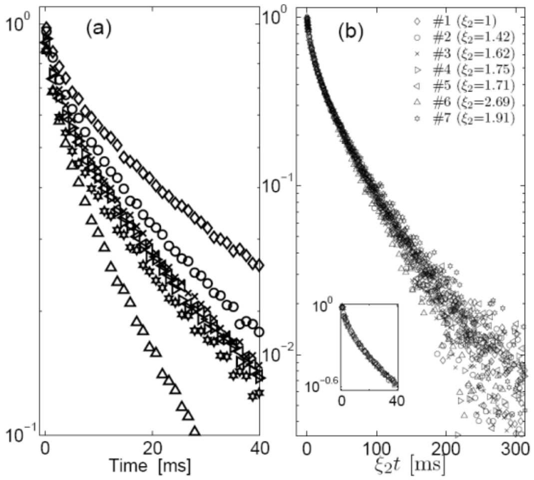

Fig. 1: (a) CPMG for seven samples with the same base oil and asphaltene concentrations from 0% (sample #1) to 11% (sample #7). (b) The same samples with time axis rescaled by constant ξ_2's (see legend). Inset shows the range from panel (a) for easy comparison.

Remarkably, the data for different asphaltene concentrations, both for T2 (see Fig. 1(b)) and for T1 relaxation (not shown), collapses onto a single decay curve upon rescaling the time domain. This is a highly nontrivial phenomenon, given the multi exponential nature of the relaxation. We have developed a simple model, based on interactions between asphaltene clusters and maltene chains, that relates the scaling coefficients ξ_2 and ξ_1 (corresponding to T2 and T1 relaxation, respectively) to the size of asphaltene clusters. Applying our formulas to the present data yielded cluster sizes of the order of 4 nm, consistent with other methods for assessing asphaltene aggregate sizes.

Chemical Resolution in T_1-T_2 correlations

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T_1-T_2 correlations are useful for determining the ratio T_1/T_2 as a characteristic parameter for permeable rocks [1]. However, the presence of both oil and water can complicate the analysis. Sedimentary rocks are therefore analyzed with D-T_2 correlations at low magnetic fields because of the distinct difference in diffusion coefficient D of the two liquids [2]. Here we present a novel T_2-T_1-δ correlation [3] where the chemical shifts δ allow the water and oil fractions to be identified; see Fig. 1.

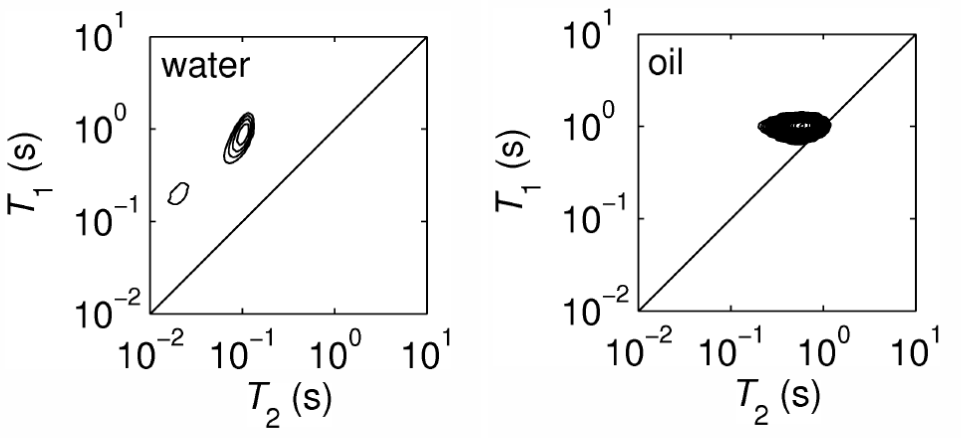

Fig. 1. Chemically resolved T_2-T_1 correlations reveal the water and oil fractions within a sandstone rock core.

The T_2-T_1-δ correlation is acquired in the same experimental time as a conventional T_1-T_2 correlation. This is achieved through the use of a "double-shot" measurement of T_1 [4], so-called because it requires the spin ensemble to be stored "up" and "down" in successive scans [5]. In this way the longitudinal relaxation information is encoded in an exponential decay (rather than a recovery). Since this T_1 measurement is based on the acquisition of multiple FIDs, chemical shift information can be extracted.

Furthermore, we propose a novel T_1-T_1 exchange measurement and demonstrate this by determining exchange between cellulose fibers at high magnetic fields where the susceptibility induced field gradients distort the traditional T_2-T_2 exchange measurements.

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NMR diffusion and relaxation studies of molecules confined inside core-shell polymeric capsules

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Understanding the surface effects on dynamics of molecules confined in nanocapsules is important both for obtaining of theoretical scientific knowledge and for designing of new nanocapsules to be used in controlled drug delivery [1]. Obtaining of information about the surface effects on confined molecules and the molecular exchange through capsules membrane can be favorably accomplished using nuclear magnetic resonance diffusometry and relaxometry techniques [2]. 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, de 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) [3] is the subject of our investigations.

In our contribution we will report diffusion and relaxation studies performed on miglyol and hexadecane molecules encapsulated in polymeric nanocapsules of different dimension. The core-shell polymeric capsules were prepared by two different methods based on emulsification – diffusion technique [4]. The diffusion experimental data obtained with a high field instrument (9.4T) using the fringe field stimulated echo (FFStE) technique [5] were compared with those obtained with a low field instrument (0.47 T) by using the well known pulsed field gradient stimulated echo (PFGStE) technique. The proton relaxation data were obtained at 20 MHz using the CPMG technique. The apparent diffusion coefficient extracted from the first part of echoes decay allowed us to evaluate the capsules dimension. The coincidence with the dimension observed from electron micrograph is remarkable. In order to obtain a correct interpretation of the experimental data these were also compared with Monte Carlo simulations.

This work was financed by the CEEX – MATNANTECH 58/2006 project. We thank Prof. Rainer Kimmich from Ulm University for allowing us to perform the FFStE measurements.

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MRI Evaluation of the Effectiveness of Colloidal Dispersion Gels for Enhanced Oil Recovery

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Sweep efficiency in mature or marginal conventional oil fields is significantly affected by fluid channeling through rock cracks, fractures, and high permeability "thief zones". Colloidal dispersion gels (CDG) have been proposed as an enhanced oil recovery (EOR) method to block deleterious fluid channeling in petroleum reservoir formations. Controversy exists in the literature however about the effectiveness of CDG.

Centric-scan SPRITE was employed to visualize the behavior of CDG in controlling fluid channeling in laboratory studies with core plug samples. The Centric-scan SPRITE method provides quantitative fluid density images in porous media that are difficult to image by conventional MRI techniques due to short transverse signal lifetimes and multi-exponential T_1, T_2 behavior.

The experimental results showed CDG is an effective technique for controlling conformance problems in porous media. Centric-scan SPRITE MRI permitted accurate monitoring of displacement fronts between displaced and displacing fluids through the porous matrix and high permeability channel.

Characterisation of pulsing flow in trickle-bed reactors using ultra-fast MRI

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Trickle-bed reactors (TBRs) are widely used in petroleum refining and throughout the chemical industry. TBRs take the form of columns packed with solid porous catalyst pellets. The most common mode of operation is with concurrent down-flow of liquid and gas reactants. TBRs can therefore be thought of as porous systems on two different length-scales; a macro-pore structure formed by the void space between the catalyst particles, which interacts with the micro-pore system of the catalyst pore structure. It has been suggested that operation of TBRs at high liquid and gas flow rates in the so-called pulsing regime, can improve the reactor performance in terms of mass, heat transfer rates and better catalyst utilisation [1, 2]. However, an understanding of the hydrodynamics within the reactor operating under these conditions has not yet been achieved. In this work, we use ultra-fast MRI techniques to characterise hydrodynamics during pulsing flow and compare these results with those obtained using conductance measurements – a technique well established for this application within the chemical engineering community [3].

This paper presents the results of ultra-fast one-dimensional (1-D) Fast Low Angle SHot (FLASH) MRI to characterise the liquid pulses in TBRs. ^{1}H MRI experiments were performed at 200 MHz on a 4.7 T magnet. 1-D liquid holdup profiles along the flow direction were acquired at spatial and temporal resolutions of 352 μm pixel^{-1} and 3.3 ms, respectively. It is demonstrated that properties such as pulse velocity, duration and frequency, obtained with MRI are in good agreement with the conductance data. MRI is shown to have three advantages compared to the traditional conductance measurement approach:

- Individual pulses are tracked and therefore the pulse velocity measured with MRI is more accurate when only part of TBR is pulsing.
- The distribution of pulse velocities is obtained as opposed to a time-averaged measurement.
- Since individual pulses are tracked, splitting of a single stream into two, and merging of two streams into one are imaged directly. Such information cannot be obtained using the conductance approach.

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Study of Miscible and Immiscible Flows in a Microchannel Using Magnetic Resonance Imaging

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Microfluidic devices have attracted much interest in the fields of biology, biotechnology, and analytical and synthetic chemistry with applications as varied as protein crystallization, analyte diagnostics, cytometry, and combinatorial chemistry. These miniaturized fluidic systems have many advantages over their macroscale equivalents and have made feasible the integration of multiple processes on one device – the so-called lab on a chip or micro total analysis system. Many attempts have been made to characterize mixing performance in microfluidic systems with a view to optimizing their design and operation. Both flow and concentration mapping have typically been achieved by using optical methods. Despite the achievements of workers using optical techniques, there remain some inherent limitations of these methods. For example, the applicability of optical methods is limited to systems that have been fabricated and sealed with optically transparent materials. Optical methods are also often limited with respect to the type of device geometry that can be studied. More recently, researchers have begun to explore MRI as a tool for the study of microscale systems[1,2,3].

In this work, MRI has been used for the first time to obtain both cross-sectional velocity and concentration maps of flow through an optically opaque Y-shaped microfluidic sensor. Images of 23 µm × 23 µm resolution were obtained for a channel of rectangular cross section (250 µm × 500 µm) fed by two square inlets (250 µm × 250 µm). Both miscible and immiscible liquid systems have been studied. These include a system in which the coupling of flow and mass transfer has been observed, as the diffusion of the analyte perturbs local hydrodynamics. Our motivation for developing MRI tools for the study of microchannels extends beyond experimental visualization of mixing performance. The data thereby obtained can be used in the validation of numerical codes for simulating micromixing processes. Such codes will play a key role in the design and optimization of microfluidic systems. Images presented in this work have been used by Sullivan *et al.*[4] to validate a lattice-Boltzmann code capable of simulating coupled diffusive mass transfer and hydrodynamics in 3D.

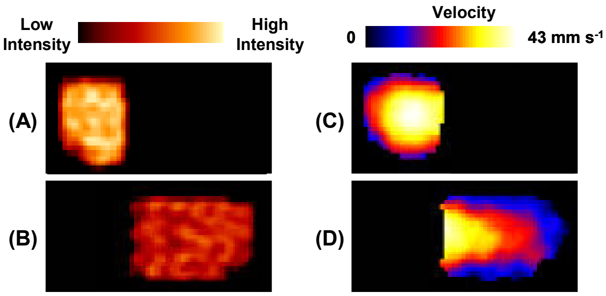

Fig. 1: Images of multiphase, immiscible flow through the microchannel. Selective saturation was used to image either the aqueous or organic phase independently. (A) Organic phase. (B) Aqueous phase. (C), (D) Velocity maps of the organic and aqueous phases respectively.

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Velocity and diffusivity mapping of water flow in a bead pack by a purely phase-encoded MRI method

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In the past years, magnetic resonance imaging (MRI) has been proved to be a valuable method for measuring flow properties. In this talk, we present a motion sensitized version of the MRI method SPRITE (Single Point Imaging with T1 Enhancement [1]) measuring fast, mechanically dispersed water flow in a pack of large glass beads (Velocity 20 ~40cm/s, Reynolds number up to 2000, Average bead size 1.6cm). This method is quantitative, three dimensional and has potential time saving over traditional pointwise techniques for measuring fluid flow. Use of a purely phase-encoded method means that the encoding interval can be kept very short, allowing greater control of intravoxel phase dispersion than many frequency-encoded techniques. The SPRITE family of techniques is essentially immune to artifacts caused by material boundaries in magnetic susceptibility. The mean velocity and turbulent diffusivity of water flow were mapped. SPRITE has great potential for future study in dispersed fluid flow and CFD (Computational Fluid Dynamics) software validation.

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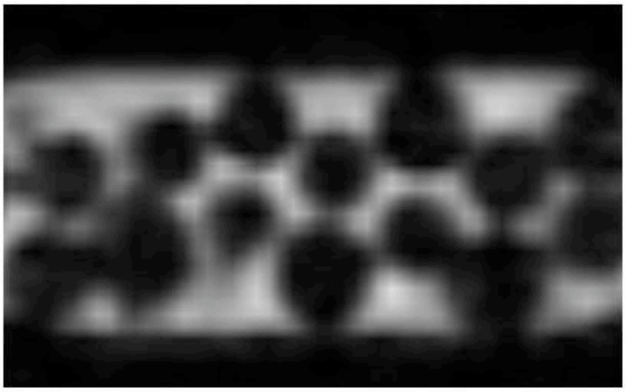

Fig: 2D slice of 3D spin density image of the bead pack, spatial resolution 64 by 64 pixels

Touching-Vug velocity and exchange with matrix pores in models and samples from the Biscayne aquifer

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We used stimulated-echo based velocimetry to measure three-dimensional steady velocity fields in the centimeter scale vugs and short echo-time spin warp imaging to study the washout of D_2O from the porous matrix. Washout experiments were done under static and flowing conditions.

The Biscayne aquifer in southeast Florida is one of the most permeable aquifers in the world.[1] The large scale macroporosity is due in part to shrimp burrows.[2] As part of a combined experimental and computational effort aimed at modeling the aquifer on many scales, we investigated the feasibility of some simple MR techniques. Figure 1 is an example that shows the almost immediate washout of D_2O from the macropores and the exchange that occurs with the water in the rock matrix over a longer time scale.

The experiments were done in a 1.89T horizontal bore system controlled by a Tecmag (Houston, TX) Libra. The 3d model used in the velocity measurements was constructed by a rapid-protoyping 3d epoxy printer. The evolution time in the stimulated echo experiments was approximately 1s, T_1 was 2.7s, flow rates were set to match the superficial velocity in the aquifer, resulting in average velocities of 0.045 cm/s and 0.025 cm/s. The higher flow rate was used in the washout experiment shown in Figure 1.

Our results show that MR imaging is a promising technique for studying flow fields and transport properties pertinent to the Biscayne aquifer.

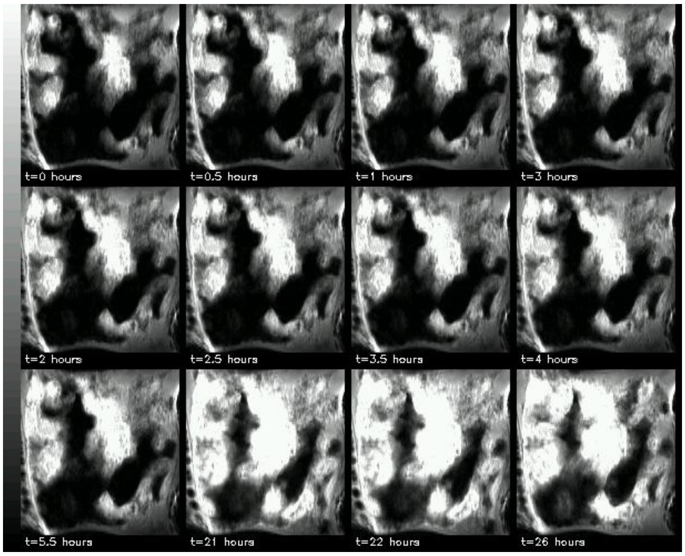

Fig. 1: MR images, FOV 8x8 cm, taken periodically show the incursion of water into an initially D_2O saturated carbonate rock (ML-3) from an outcrop near Biscayne Bay.

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Viscosity Prediction in Polymer Melts using low field NMR Relaxation

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For many viscous liquids, NMR relaxation techniques can be used to estimate viscosity. However, the usual semi-empirical correlations fails in polymer melts due to their specific molecular dynamic. We present a combined viscosity-NMR study on a model system composed of linear polymers of increasing molecular weight (Polyethylene glycol, PEG). We show that the system studied behaves as expected for cross-linked polymers[1]. Viscosity, longitudinal and transversal relaxation times T_1 and T_2, and diffusivity clearly show the entanglement transition at M_c~3000 g/mol and the expected power law dependences are verified for viscosity ($\eta \propto M_w^3$) and diffusivity ($D \propto M_w^{-2}$). However, for polymer melts, the standard viscosity prediction from T_2 relaxation data ($T_2 \propto (\eta/T)^{-1}$) is not valid. In addition, T_1 does not vary with viscosity when varying the molecular weight although it varies with temperature.

We interpret these experimental data in the framework of a two correlation time model and we used the spectral density function proposed by Lipari and Szabo[2]. The T_1 and T_2 viscosity and temperature dependence is due to a different sensitivity to fast (local) and slow (global) motions of the molecules. The different time scales of the system can be deduced from the measured quantities D, T_1, $T_{1\rho}$, T_2. In the present case, the order parameter S of the Lipari-Szabo model is linked to the proton fraction involved in the entanglements. We propose a new predictive model for viscosity combining T_1 and T_2 (Fig. 1).

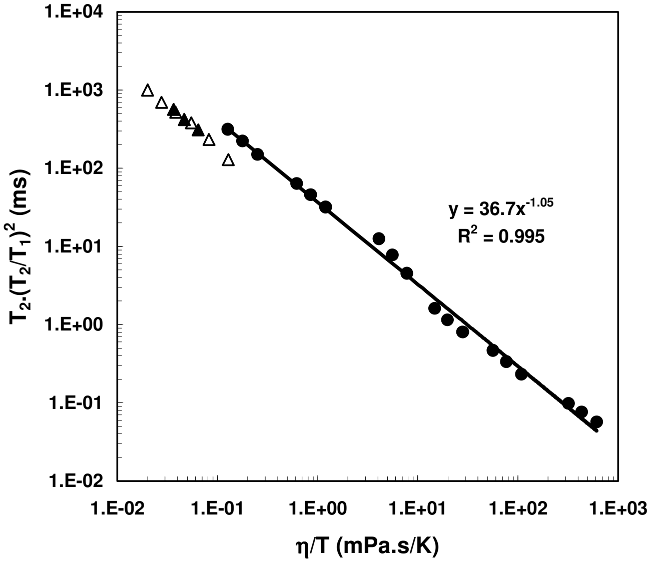

Fig. 1: Viscosity prediction valid for entangled polymers (full circles); the prediction can also be used for non entangled polymers (triangles, $T_2/T_1 \cong 1$) but with a different pre-factor. This relation has been established on PEG samples of molecular mass M_w varying from 200 up to 35 000. For each molecular mass, the temperature was varied from 60 up to 80°C.

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Diffusion tensor micro-imaging of articular cartilage as a probe of tissue microstructure

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Osteoarthritis is a disease of articular cartilage that affects an estimated 20% of the population, but the early stages of osteoarthritis are difficult to diagnose and the progression of the disease is poorly understood. Articular cartilage covers the ends of the bones in joints, providing a smooth low friction surface that absorbs shocks and distributes load to the subchondral bone. Healthy adult human cartilage is 2-4 mm thick and has a complex composition and structure. It contains collagen (15–20%), proteoglycans (PG, 3–10%), lipids (1–5%), chondrocyte cells, and water (65-80%). The collagen forms a cross-linked network, in which three zones of alignment are usually distinguished: the fibres at the articular surface are aligned parallel to the surface and become increasingly aligned normal to the surface at greater depth. Collagen is primarily responsible for the compressive stiffness of cartilage, while the PG's are responsible for maintaining osmotic equilibrium.

Cartilage is invisible on plane x-rays and its thickness can only be inferred from the separation of the subchondral bone surfaces. The surface of the cartilage can be viewed using arthroscopy, but this is invasive and provides no information on changes in structure and morphology of the cartilage beneath the articular surface. In conventional clinical MRI the appearance of cartilage is complicated by the presence of bands of high and low signal intensity that depend on the orientation of the normal to the articular surface with respect to the applied static magnetic field. These bright and dark bands reflect the orientation dependence of the spin-spin relaxation time T_2, which is determined by constraints on the mobility of water protons imposed by the underlying structural anisotropy of the collagen fiber matrix. Thus, while the complex nature of contrast observed in clinical MRI of cartilage has to date been seen as a complicating factor for diagnosis, MRI has the potential to provide information on changes in molecular structure of cartilage that could assist in the early diagnosis of disease and in monitoring response to therapy.

In studies of bovine cartilage *in vitro*[1,2] we have shown that diffusion tensor imaging (DTI) can be used to monitor the orientation of the collagen fibers as a function of depth from the articular surface and to measure changes in fiber orientation produced by both enzymatic degradation and mechanical compression. Results were correlated with data from polarized light microscopy (PLM)[3] and polarized Fourier transform infra-red spectroscopy (FTIR). We are currently modeling the orientation dependent relaxation of protons on water molecules bound to collagen fibers with a view to correlating T_2 anisotropy with molecular sub-structure in cartilage.

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Role inversion in magnetization exchange between water and macromolecular protons in articular cartilage components at different hydration levels

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NMR techniques are acquiring an ever-increasing importance both in basic science and clinical studies of articular cartilage, a connective tissue that can be considered, for many aspects, as a porous medium. NMR is unique as it furnishes non-destructive tools to evaluate the changes occurring in the cartilage due to pathologies and ageing, both in vitro and in vivo. In particular, MRI can be repeatedly used to monitor changes of articular cartilage of the human joints, without radiation damages. One of the most relevant MRI parameters is the magnetization transfer rate, that has been related to the concentration of the collagen fibres.

We studied the exchange of magnetization between water and macromolecular protons both ex vivo in native cartilage, and in its purified components, collagen and proteoglycans, at different water content. All the free induction decays could be fit by the sum of an exponential (liquid-like) and a Gaussian or modified Gaussian (solid-like) signal. The "solid-like" component is due to macromolecular ^1H of restricted mobility, the "liquid-like" to water. When quasi-continuous distributions of longitudinal relaxation time were computed without imposing the usual non negativity constraint, the effect of the magnetization exchange between macromolecular and water ^1H was evident. Data could be formally fit by a simple two-site exchange model, already used by us for a study of hydration in seasoned woods[1], where the Solid-to-Liquid exchange times were found to be of the order of few tens of ms. An inversion of the Solid-Liquid roles in the magnetization exchange was observed with changing the hydration level of the macromolecules. Such an inversion has been seen to occur at the hydration level 20-26% (w/w) in a model system (Sephadex G10)[2].

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GARField NMR profiling studies of human *stratum corneum* and viable epidermis *in vivo*

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In a series of recent papers[1] describing a limited number of trials, we have shown how GARField magnetic resonance profiling is an ideal tool to study small molecule transport in human skin *stratum corneum* and viable epidermis both in-vitro and in-vivo. This is possible because, with GARField, the resolution (pixel size) is better than 10 μm with a first echo time as short as 150 μs. In this previous work, there was indication that profiling of magnetic relaxation parameters can access the qualitative parameter that is often dubbed "skin-moisturisation": this being a reflection of skin suppleness rather than true hydration. The current work described here goes forward with two objectives.

In one set of experiments, a 5 pulse sequence (P_{90} - $(\tau-\delta)/2$ - P_{180} - $(\tau+\delta)/2$ – P_{90} - Δ - $(\tau+\delta)/2$ - P_{90} - $(\tau-\delta)/2$ – P_{180} - echo) has been used to measure self-diffusivities in *stratum corneum* and viable epidermis *in vivo* under the constant gradient conditions of GARField[2]. This sequence allows simple diffusion of a single species to be measured independent of relaxation weighting using constant τ and Δ intervals. By sampling the full 3 dimensional parameter space, δ, τ, and Δ measurements of more complex diffusion scenarios with different characteristic length scales as a function of time are possible. On human *stratum corneum* and viable epidermis these experiments reveal (for the first time and *in vivo*) diffusion of water in a spatially and temporarily defined manner showing different characteristic behaviours.

In other experiments, we quantitatively compare changes in *stratum corneum* and viable epidermis relaxation rates occurring as a result of the application to the skin of materials typical of model skin care formulation systems, with changes in the more standard measurement of trans-epidermal water loss and with corneometer testing. Excellent correlation between the results of the different methods is found. In one particular study, the volunteer ate a light meal and took moderate exercise during the trial. These activities are known to affect core body temperature and skin hydration and are faithfully echoed in the data sets. Single-point signal-to-noise ratio and bio-reproducibility are comparable between the different methods. However, the GARField MR alone provides depth resolution within the skin layers and has allowed a simple qualitative model of skin swelling and moisturisation to be inferred.

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MRI VISUALISATION OF THE MOISTURE INGRESS INTO POROUS TISSUE OF THE DECAYED TEETH

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Introduction: During last decade MRI has been used in the research of the healthy and decayed teeth for visualization of the dental surface geometry as well as for distinction between soft tissue (pulp) and mineralized tissue (enamel, dentine and root cement) in the extracted teeth [1-3].

The aim of this work was to asses applicability of different MRI techniques for detection and visualisation of the water ingress into porous structure of the decayed teeth *in vitro*.

Materials and Methods: Five extracted human teeth with different level of decay were used for 3D Spin Echo (SE) MR Imaging done in MR Tomography Lab INP, Krakow, Poland, using 4.7 T research MRI system. 3D (512x128x128) images of the teeth with resolution of 30x120x180 μm^3 were obtained.

Single Point Imaging (SPI) [5] were performed using 11.7 T, vertical bore Bruker MRI system, in IBD, Winnipeg, Canada. In this case resolution of 315x315x940 μm^3 was achieved.

MR data were visualized and analyzed using home developed IDL based software and ImageJ software.

Results

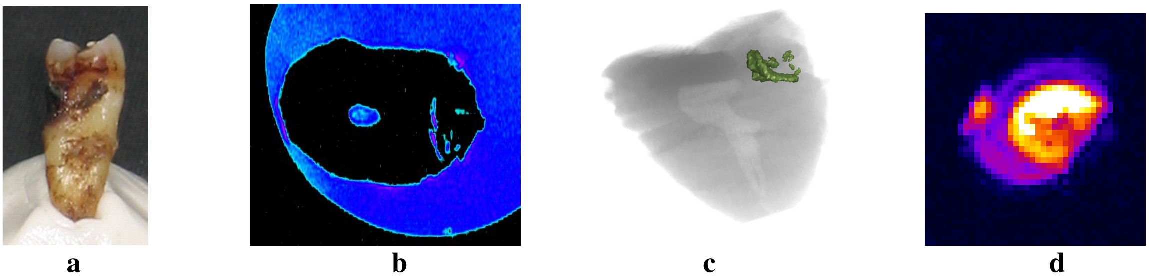

Fig.1 The photo image (a), corresponding cross-sections through 3D SE MR image (b) and the pseudo 3D reconstruction (c) of the water in porous tissue of decayed tooth, obtained from 3D SE MR data. In fig (d) 2D cross-section from 3D SPI data of tooth with decay comparable to that for SE images is shown.

Discussion & Conclusions: Spin-echo based MR imaging methods allow for high resolution visualization of the moisture entering into heavily decayed tooth, which are paths for microorganisms causing further damage of the tissue. With this methods it is not possible to see any details in mineralized tooth's tissue, especially gradual decrease in tissue density in early stages of the caries development. With this respect, the SPI method which allow for visualization of the mineralized tissue is more promising.

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Correlated analysis of the diffusion and T2 relaxation of water in multi-compartmental tissue of the spinal cord of a rat

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Introduction: Present understanding of water diffusion in nervous tissue is based on assumption of three water compartment: intra-cellular, myelin and extra-cellular, with different diffusion and relaxation characteristics. There is still lot of debating concerning details of the diffusion model which includes all three compartments. To clarify this, proper characterization of all compartments is necessary. Especially myelin water is difficult to detect due to short T2. The aim of this work was to set up protocol for combined diffusion/relaxation characterization of all three compartments.

Subject and Method: The male Wister rats used for measurements were anaesthetised using halothane in oxygene. MR measurements were performed on the 4.7 T research tomograph equipped with Maran DRX (Resonance Instruments Ltd.) console and the home built gradient coils and the surface coils. ECG and breath triggered 3D spin echo (SE) sequence without slice selection was used to measure diffusion for *b*-values up to 30000 s/mm^2 and for different echo times (TE) in range from 10 ms to 400 ms.

Results: The diffusion weighted MR images (128x128) of the spinal cord as a function of *b*-values were obtained for range of TE values. Dependence of signal amplitudes on TE and *b*-values for directions perpendicular and parallel to the spinal cord axis for white matter and gray matter were assessed and described in terms of multi-exponential as well as continuous 2D distribution of the T2/diffusion decays.

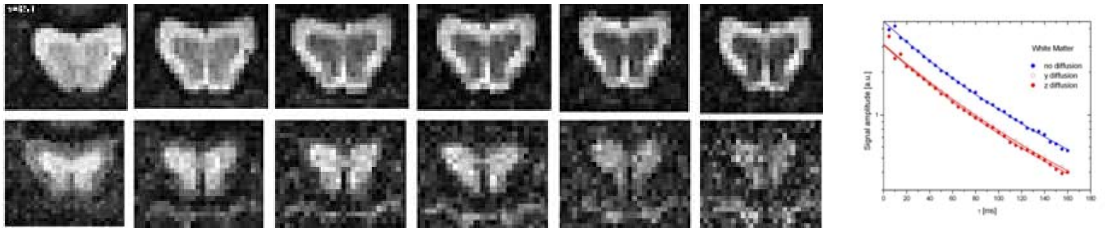

Fig.1. (a) MR images of the spinal cord of a rat in vivo with diffusion gradients oriented in direction perpendicular (top) and parallel (bottom) to spinal cord axis, for b equal to: 650, 1300, 1800, 2300, 2800, 3300 s/mm^2; (b) T2 decays in white matter for the diffusion gradients perpendicular to the axis of the spinal cord.

Diffusion decays in direction along spinal cord are close to mono-exponential, especially in WM. Diffusion in direction perpendicular to spinal cord axis deviates substantially from mono-exponential (Fig 1b).

Discussion/Conclusions: 3D Spin Echo based sequence was found useful in characterisation of diffusion in different water compartments in nervous tissue, due to possibility of measurements with short TE. Observed dependence of diffusion/relaxation decays on TE was attributed to compartmentalisation of the water within nervous tissue.

Acknowledgments:

This work was partially supported by research grant no. 1 P03B 009 28 from Ministry of Science and Informatisation of Poland and European Reintegration Grant no. 46386.

In vivo imaging of DDIF contrast in the Human Knee

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Trabecular bone (TB) is a porous structure found in load-bearing skeletal regions and joints (vertebrae, radius, femur, calcaneus), and is monitored to determine risk of fracture or osteoporosis. However, the clinical densitometry standard fails to account for half of fragility variations, and diagnostics that incorporate architectural "bone quality" information are in high demand(1).

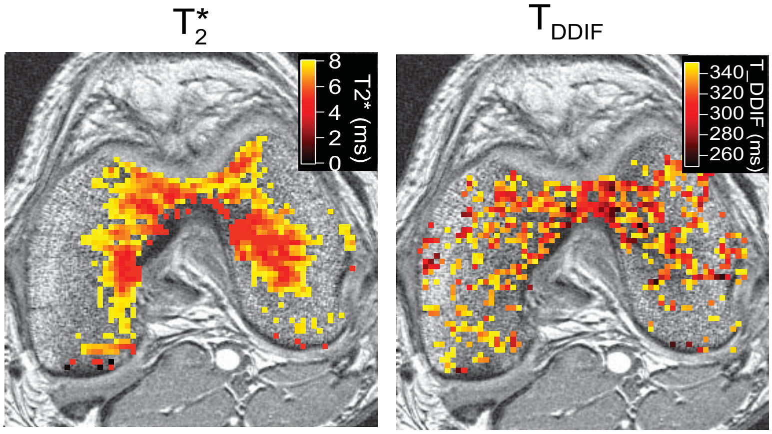

Figure 1: T_2* and T_{DDIF} (t_e = 40 ms) contrast in an axial slice of a healthy volunteer distal femur at 3 T. Windowed parameter maps are overlaid on a high resolution FLASH image.

Recent *in vitro* work has applied an MR structural contrast—decay from diffusion in the internal field (DDIF)—to trabecular bone, including both bulk measurements(2) and microimaging(3) over a wide range of structure and strength. This work showed that DDIF probes the projected surface-to-volume ratio along the applied field. The present study extended this technique to the first *in vivo* DDIF contrast results in healthy human volunteer knee joints.

Imaging was performed in a full body 3 T Siemens Trio scanner with a single channel CP knee coil. Four healthy volunteers were scanned with an imaging protocol including a FLASH-3D scan for high resolution anatomical reference (0.3 x 0.3 x 1.5 mm), gradient echo imaging at variable echo time for T_2* mapping, inversion recovery prepared turbo spin echo imaging at variable inversion time TI for T_1 mapping, and a stimulated echo prepared BURST imaging at variable mixing time t_D for DDIF mapping. The parametric maps were acquired at 1.2 x 1.2 x 3 mm resolution. T_2* and T_{DDIF} maps were generated by single exponential fitting, and T_1 maps by single exponential recovery fitting.

Figure 1 shows a comparison of the short decay time limits of T_2* and T_{DDIF} maps in an axial slice through the condyles of the distal femur. Both show high contrast in the intercondylar notch, where trabecular density and mechanical stresses are high. Beyond this commonality the two spatial patterns are similar but not identical. Higher precision (e.g. higher SNR sequence) will be required to explore the unique sensitivity of DDIF. However, this pilot study confirms that DDIF probes trabecular structure *in vivo*.

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Helium Diffusion Kurtosis MRI of the Lungs

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Diffusion MRI of hyperpolarized ^{3}He is a promising method of characterizing the small airspaces (1). Diffusion is restricted by lung structures and hence measured diffusion coefficients reflect airspace size. However, with typical diffusion times of a few milliseconds (limited by the short T2* of helium) diffusion measurements largely reflect alveolar size and are insensitive to changes in the bronchioles. Diffusion kurtosis imaging (DKI) measures the degree to which diffusion is non-Gaussian and is particularly sensitive to diffusion over larger distance scales (2). Including the kurtosis term MR signal intensity is

$$S = S_0 \exp\left(-bD + \frac{1}{6}b^2 D^2 K\right)$$

where S_0 is the signal intensity without diffusion weighting, b is the diffusion weighting constant, D is the diffusion coefficient and K is kurtosis (2). Kurtosis can thus be measured with conventional diffusion imaging sequences with at least three b-values.

DKI was performed on five normal controls and three firefighters involved in the rescue attempts at the World Trade Center. The firefighters suffered from symptoms including cough, wheezing, shortness of breath, chest pain, and dyspnea. Gradient-echo diffusion images were acquired on a 1.5T scanner (flip-angle 4°; matrix 80×128; slice thickness 15mm; FOV 330×380mm; TE 11ms; TR 14ms; b= 0,3,6,9,12 and 15s/cm^2).

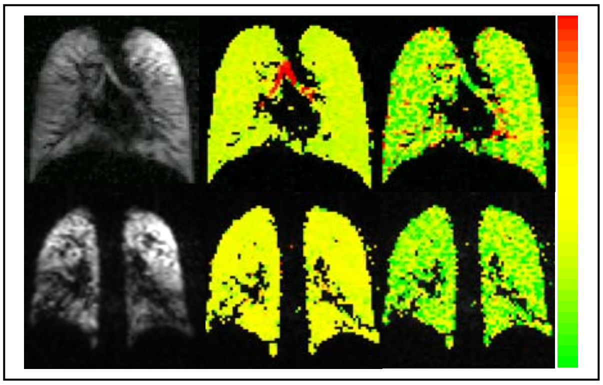

Fig. 1. Coronal images of a normal control (top) and firefighter (bottom) with evidence of small airway disease. Left: ventilation images. Middle: Diffusion coefficient maps (range 0.0 – 0.6). Right: Diffusion kurtosis maps (range 0.0 – 1.0). Diffusion is similar in both subjects but kurtosis is reduced and less heterogeneous in the firefighter.

Measured parameters were: firefighters D=0.263±0.049, K= 0.213±0.022; controls D=0.337±0.038, K=0.212±0.024. Although there was no statistically significant difference in the D (p=0.95), the firefighters had a substantially reduced K with a p value approaching significance (p=0.098).

Decreased kurtosis in combination with normal diffusion coefficients suggests bronchiolar constriction in the firefighters, an interpretation supported by the finding of air trapping demonstrated by CT.

DKI may provide information that is complementary to that provided by conventional diffusion imaging.

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Toward accurate and precise S/V measurements of lung airspaces using noble-gas diffusion NMR

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In-vivo diffusion measurements can be made in lung airspaces using gaseous NMR signal sources such as hyperpolarized ^{3}He or ^{129}Xe. Whereas the relatively large self-diffusivity of these noble gases is an advantage for accessing long length scales corresponding to the tortuosity limit in porous solids, it a disadvantage for accessing short length scales corresponding to the surface-to-volume ratio (S/V) of lung airspaces [1]. For noble-gas diffusion in normal human lung, extracting S/V values from the short-time-scale limit of the time-dependent diffusivity curve requires that the curve be sampled at diffusion times much less than a millisecond [2]. This requirement generally precludes the use of refocusing RF pulses between individual lobes of the diffusion-sensitizing gradient, and also makes it impractical to generate measurable NMR signal attenuation using narrow gradient pulses. Although quantitative corrections can be applied that compensate for systematic errors resulting from the use of wide gradient pulses [3,2], it is nonetheless difficult to make clean diffusivity measurements subject to these constraints.

We recently developed a new gradient-echo-based pulse sequence for measuring noble-gas diffusion, which provides improved measurement accuracy and precision at sub-millisecond diffusion times [4]. These advantages were demonstrated using both Monte-Carlo simulations and phantom measurements in simple pore geometries. We are currently exploring the ability of our technique to quantify S/V in the pore space between loosely packed microspheres, using ^{129}Xe gas at atmospheric pressure. A significant component of this effort is to characterize the effects of susceptibility-induced background gradients on the measured diffusivities. Taken as a whole, these developments represent a significant step toward establishing the feasibility of making reliable in-vivo lung S/V measurements using NMR of noble-gas diffusion.

This research was supported by NIH grants R01-HL079077 and R21-HL089525, and by Siemens Medical Solutions.

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Human Pulmonary Function with Hyperpolarized ^{129}Xe

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The function of the lung is gas exchange; avelolar oxygen diffuses into blood and CO_2 diffuses in the opposite direction. This is accomplished by the lung's large surface area (~100m^2) due to its fine porous structure together with a thin septal barrier separating alveolar gas and capillary blood. Here, we describe a noninvasive method to determine three functional components of the lung: alveolar surface area per unit volume of gas (*S/V*), which decreases in emphysematous disease; septal thickness *h*, which increases in interstitial disease; and capillary transit time τ, important for vascular diseases.

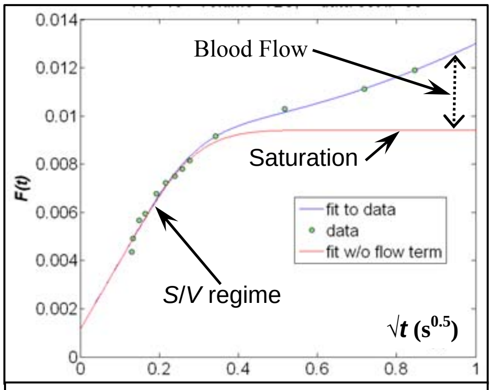

Figure 1. Example of human CSSR data.

The spectrum of ^{129}Xe in the lung exhibits a gas peak at 0ppm and dissolved state peaks at ~+200ppm. A chemical shift saturation recovery (CSSR) pulse technique is used to first saturate the dissolved phase ^{129}Xe magnetization and then observe its recovery[1] due to diffusion of magnetized ^{129}Xe from the gas spaces to the septa. The fraction *F* of the dissolved state signal at time *t* after the saturation pulse relative to the initial gas phase signal is measured. The data is fit to an analytical form obtained from the solution of a 1D diffusion geometry and includes a constant velocity blood flow term. Input parameters to the model are the diffusivity of ^{129}Xe in tissue and the Ostwald solubility. Fitted parameters are pulmonary S/V, *h*, and τ. Figure 1 shows sample data from a healthy human subject after inhalation of 1L of 86% enriched ^{129}Xe polarized to ~50%. The field strength is 0.2T. Data (green points) are acquired in a 10s breath-hold. The fitted curve is shown in blue. A red curve, calculated by setting $\tau \rightarrow \infty$, shows septal saturation in the absence of blood flow, where the saturation value depends on *h*. The early time behavior is $\sim\sqrt{t}$ and allows determination of *S/V*[2].

To obtain this type of information regionally, we modified the XTC method[3] to a single breath-method[2]; each experiment produces a map of *F* at a single *t*. Figure 2 shows 3 gradient echo images serially acquired (a-c). Signal attenuation between images is due to (r_1) RF depletion of the nonrenewable hyperpolarization, (r_2) T_1 decay due to oxygen, and (r_3) interphase diffusion. Attenuation between (a) and (b) allows determination of r_1r_2. Between (b) and (c), attenuation = $r_1r_2r_3$ where r_3 is enhanced due to multiple applications of $[180^o_{\mathrm{dissolved}} - t]$ between the two images. Determination of r_3 allows calculation of *F* (Fig 2d). A separate breath of ~1L of hyperpolarized ^{129}Xe is required for each time point to acquire data similar to Figure 1 for each voxel. This work was supported by NIH RO1 HL073632.

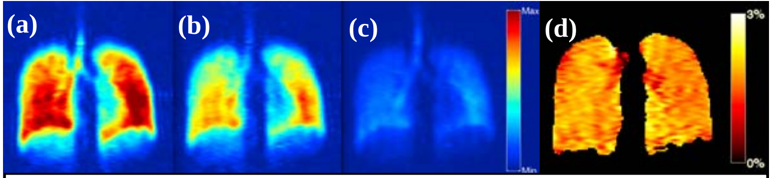

Figure 2. Example of single breath XTC for *t*=62ms. (a-c) serially acquired gradient echo images (d) calculated *F*(*t*) map.

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Magnetic Resonance Microscopy application to Biofouling in Porous Media

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From water service utilities to pharmaceutical processing, biofilms either create havoc or are crucial to the system function in almost every water-based industrial process. In subsurface bioremediation, biofilm establishment and maintenance is crucial to many processes intended to degrade or contain contaminants. Many of these situations in which biofilm growth needs to be understood involve water transport in a growth medium that can be interpreted as a porous media. Thus, there is an urgent need to better understand the structure and transport changes that occur in biofouled porous media. Magnetic Resonance Microscopy (MRM) techniques have been used to study the effective change in pore structure and pore connectivity due to biofilm growth and the impact this growth has on transport phenomena. The porous media used in this study are model beadpacks constructed from various glass and plastic spheres with diameters between 100-300 μm.

MR spectral characterization of diffusion with chemical shift resolution: study of highly concentrated emulsions

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Emulsions are important for many technological applications for example in pharmacy as drug delivery systems and in food or cosmetic products. Diffusiometry is a well-established approach to study morphology of porous materials and emulsions. Self-diffusion of different substances in highly concentrated water-in-oil emulsions have been studied by the pulsed gradient technique [1]. In the case of fairly mono-dispersed emulsions the diffraction pattern of signal intensity vs. phase factor q can reveal the information about droplet size. The effects of finite length gradient pulses in characterising emulsions have been thoroughly examined [2].

The finite gradient pulse effects are not relevant to the modulated gradient spin-echo method (MGSE) [3,4]. It provides information about molecular diffusion in frequency domain. Instead of using gradient pulses it employs harmonically oscillating gradients. This results in spin-echo attenuation, which is proportional to the spectrum of velocity autocorrelation function of the spin-bearing particles. The effect of spin de-phasing, due to diffusion, is accumulated over many gradient oscillation cycles, giving rise to adequate diffusive attenuation on a shorter time scale compared to the pulsed field gradient method.

We present an application of the MGSE method, which uses sinusoidaly shaped gradient pulses separated by 180-degree RF pulses. This produces an apodized cosine gradient modulation waveform, similar to the one employed by Parsons et al. in combination with imaging [5]. The RF pulses used in the presented technique efficiently refocus chemical shifts and de-phasing due to susceptibility differences, resulting in undistorted, high-resolution diffusion weighed spectra. This allows for simultaneous study of several molecular components with different chemical shifts.

The method was used to study highly concentrated water-in-oil emulsion, which consists of 95 wt% 0.2 M tetramethyl ammonium chloride (TMACl) in Millipore water as aqueous phase, 3.5 wt% heptane as oil phase and 1.5 wt% Brij 92 as surfactant. The droplet size is fairly mono-dispersed around 3.3 μm. In the range between 1-20 ms we observe the transition from restricted to free diffusive behavior of water and TMACl, while oil diffusion is occluded but Gaussian.

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Pore surface of cellulose as studied by Low-Resolution NMR

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Polysaccharides are frequently considered as sorbents since they possess good absorbent ability due to branchy porous structure. The question of saccharides supermolecular organization is controversial so far, so the conception of its porous structure is not absolutely clear. Supramolecular organizations of polysaccharides is normally considered as a combination of crystalline part with well-ordered, highly oriented and densely packed macromolecules and amorphous part which is presented as a less ordered and the most reactive region. Further on we suggest that so-called "surface" region of the sample consists of atoms of glucopyranose ring which are situated on the surface of crystallites and they form nearly all the amorphous part. "Internal" regions of polysaccharides are densely packed areas with crystal-like behaviour. Surface between crystallites constitutes pores which have mainly fissured form. So it could be supposed that amorphous part organizes porous structure of polysaccharide.

Due to last tendencies NMR relaxation is very convenient method for investigation of polysaccharides sorption ability and our study basically oriented to exploit this method.

Acquired for cellulose decay contains quickly falling component, which corresponds to crystallites and slowly falling component which is referred to amorphous phase of polysaccharide. FID data potentially could be used for determination of cellulose crystallinity extent and for its porosity evaluation. But the difficult task of the FID data interpretation is caused by impossibility of satisfactory fitting of the decay.

The Fourier transformation of FID signal measured on the shift from resonance frequency offers more informative data. Doublet line width $\Delta\omega^{doubl}$ is referred to rigid lattice protons of ordered regions with low mobility. Central peak, which is narrower ($\Delta\omega^{CP}$) comprises contributions of reorienting parts of macromolecules in amorphous phase and adsorped water signal.

The central peak of cellulose spectrum has a complicated form. There are two wide lines, which are observed in condition of high magnetic field stability and large number of scans. The explanation of this fact requires additional scientific investigations. In our work different types of cellulose were treated with heating processing at the range of temperatures from 106ºC to 136ºC. Crystallinity extent, which is the most prevalent and the most studied characteristic of polysaccharides structure, finds good correlation with the height of central peak. While the temperature of treatment increasing the amplitude of central peak is decreasing.

Time of spin-lattice relaxation is the characteristic of structural order. It flows from the crystallites, where it goes slowly, to flow-out centers of magnetization located on the surface. So the longitudinal relaxation T_1 is bound up with crystallinity extent. Our investigations show obvious dependence the relaxation time T_1 on crystallinity extent. The higher crystallinity extent the greater T_1 value.

Crystallinity extent and the dimensions of crystallites determine the porosity of cellulose. The overall amount of pores is reduced with crystallites dimensions rise. There is a possibility to predict both the sorption ability and pore volume of cellulose and its crystallinity extent.

Thus proton magnetic longitudinal and transverse relaxation measurements turn to be a promising tool to determination of porous structure of natural sorbents like polysaccharides.

Spatial Microheterogeneity of Polyelectrolyte-Protein Coacervates revealed by ^{1}H Pulsed Field Gradient NMR Diffusion Study

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Polyelectrolyte-protein coacervates are dense macromolecular solutions composed of a protein and an oppositely charged polyelectrolyte. Coacervates can be used in such applications as micro-encapsulation of active food components, active drug ingredients or enzymes, since all essential properties of proteins remain preserved in the coacervate environment. Understanding the structure of coacervates on the submicrometer length scale is of importance for using coacervation to its fullest potential. Here, we report the results of pulsed field gradient (PFG) NMR studies of diffusion in coacervates formed from a globular protein (Bovine Serum Albumin) and poly(diallyldimethlyammoniumchloride), a narrow weight distribution cationic polymer. High magnetic field gradients (up to 30 T/m) were used for the observation of polyelectrolyte diffusion in coacervates on the length scale as small as 100 nm. Diffusion properties of polyelectrolyte in coacervates formed at different pH and ionic strengths have been investigated. Our results indicate the presence of dense domains with sizes in the range of 100 nm and larger formed by the protein and the polyelectrolyte. These domains were observed to be in a process of constant formation and breakup on a time scale of milliseconds. The domains are surrounded by a continuous dilute phase, which is characterized by a lower concentration of both species. These results represent a significant step towards understanding the structural and dynamic properties of coacervates on the nanoscale.

Pore Opening and Closing in Biodegradable Polymers and its Effect on Mass Transport Studied by NMR Cryodiffusometry

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NMR cryodiffusometry has been used to study the structural evolution of poly(lactic-co-glycolic acid) (PLGA) microspheres prepared by a double emulsion (w/o/w) technique. The mass transport of water within the polymer matrix was studied as a proxy for the mobility of small drug molecules entrapped for controlled release. Over time, it was found that the matrix 'pores' open and close as a result of water ingress between the polymer chains constricting pores and forcing water into new spaces. In cryoporometry, the freezing curve is often neglected due to a lack of clear understanding of hysteresis mechanisms. However, in our previous work [1], we have shown that this curve can provide information on pore neck sizes. Figure 1 shows the temporal evolution of the bimodal neck size distribution following immersion of microspheres. The neck size for the major peak first shrinks and then grows, while the minor peak grows in intensity but remains at a constant neck size. It is likely that the evolution of the neck sizes for the matrix pores controls the mobility of drug molecules within the matrix, and therefore influences the drug release profile [2]. The melting curve pore size distribution remains unchanged over the same period (not shown).

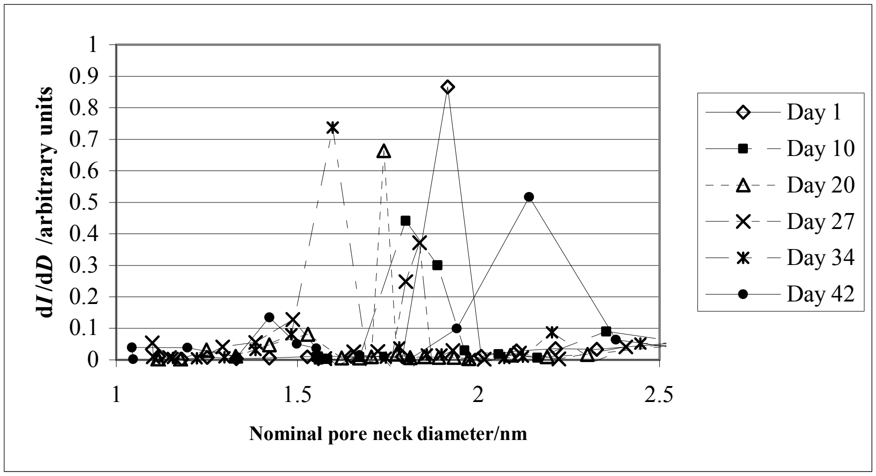

Fig. 1: Temporal evolution of the nominal diameter (D) pore necks of the PLGA matrix.

Results from cryodiffusometry experiments for molten aqueous phase solely within the polymer matrix gave rise to curved log-attenuation plots, suggesting a heterogeneous system, which fitted well to a two-component model. Hence, two distinct diffusive environments exist for water within the polymer matrix pores. Currently the drug release mechanism from PLGA microsphere systems is not fully understood, but with the additional use of cryodiffusometry, a rich data set can be found to enhance the understanding of these complex systems to improve the design of controlled drug delivery systems.

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Temporal correlation function around spheres and cylinders

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Introduction: Signal attenuation in NMR is partly due to incoherent dephasing of nuclear spins. This could be caused by independent stochastic motion of nuclear spins in inhomogeneous local magnetic fields, e.g. created by magnetized objects or voids inside magnetized bulk materials. If the magnetization time decay is not monoexponential the description with the transverse relaxation time T_2^* as single parameter will poorly describe the signal and the underlying geometry of the magnetic field.

Another way to describe the effects of diffusion is in terms of a correlation function [1]. Since it was demonstrated recently that the frequency correlation function of nuclear spins can be measured directly in NMR experiments [2], a theoretical analysis of such functions is of paramount interest.

Methods and Results: In this work we provide a numerically exact analysis of that correlation function $K(t)$ for restricted diffusion in the inhomogeneous field around cylinders and spheres (cf e.g. Fig. a). With the local larmor frequency $\omega(\mathbf{r})$ and the probability density $p(\mathbf{r},\mathbf{r}_0,t)$ to find a spin after time t at position $\mathbf{r}$ if it started at $\mathbf{r_0}$ $K(t)$ is given as

$$K(t) = \frac{1}{V}\int_V \mathrm{d}^3\mathbf{r} \int_V \mathrm{d}^3\mathbf{r}_0 \; \omega(\mathbf{r})\, p(\mathbf{r},\mathbf{r}_0,t)\, \omega(\mathbf{r}_0)\,.$$

V is the diffusion volume. $K(t)$ is solved in terms of a spectral expansion of $p(\mathbf{r},\mathbf{r}_0,t)$.

The functional form may exhibit 3 regimes: after an initial transient an algebraic regime with a $t^{-d/2}$ time dependence - d being the space dimension - may form followed by an exponential cutoff due to finite system size effects. The main parameter controlling the formation and range of the regimes is the volume fraction of the magnetic inhomogeneities. Comparing the algebraic regime with the case of long time behavior in unrestricted diffusion equal time behavior is found and can be used at this time scale. The results obtained in this work may have implications on data analysis and interpreting results and could help choosing a proper fit function for better parameter estimation.

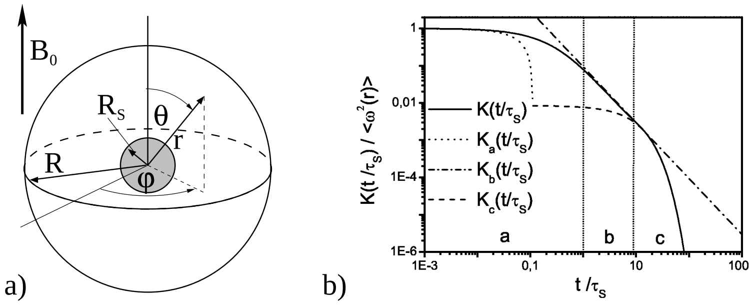

Fig. **a)** Scheme of a spherical inhomogeneity inside a spherical voxel **b)** Scheme of a double logarithmic plot of a correlation function for this geometry (K exact, K_a short time limit from unrestricted diffusion, K_b long time limit from unrestricted diffusion, K_c exponential cut off from restricted diffusion, τ_S correlation time, a, b and c denotes the different regimes)

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ANAHESS, a new second order inverse Laplace transform algorithm

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Keywords: inverse Laplace, Hessian, discrete solution, analytical expressions

The operation known as the Inverse Laplace Transform (ILT) is frequently applied in the numerical analysis of nuclear magnetic resonance experiments. Estimates of properties such as pore size distribution are frequently made on the basis of numerical ILT operations. Good ILT algorithms are therefore essential when extracting physical information from NMR experiments.

The ILT is the decomposition of a response curve in the first order case (1D-ILT) or a response surface in the second order case (2D-ILT) into a sum of exponentials. It is well known that this problem is ill conditioned, and that interpretation of the results should be considered with caution.

The aim of our research was to develop an algorithm which performs 2D-ILT with minimal assumptions, and produces models that are as simple as possible. We have constructed an inverse Hessian (or Gauss-Newton) algorithm with analytical expressions for the gradient and the Hessian matrix. Non-negative constraints are implemented by defining ILT parameters as squares of the working variables in the minimization problem.

We propose a new algorithm called ANAHESS which computes 2D-ILT with a specified number of discrete exponential components. Comparative studies show that the sum of squared errors gets lower with a fewer number of components when using ANAHESS than with a state of the art continuous distributions algorithm.

Given the premise that the ILT is ill conditioned, our conclusion is that numerical solutions to ILT problems should be as simple as possible, with discrete components rather than estimates of continuous distributions.

Uncertainties in the Assignments of Rock Porosities Obtained from Laplace Inversion of NMR Relaxation Logs

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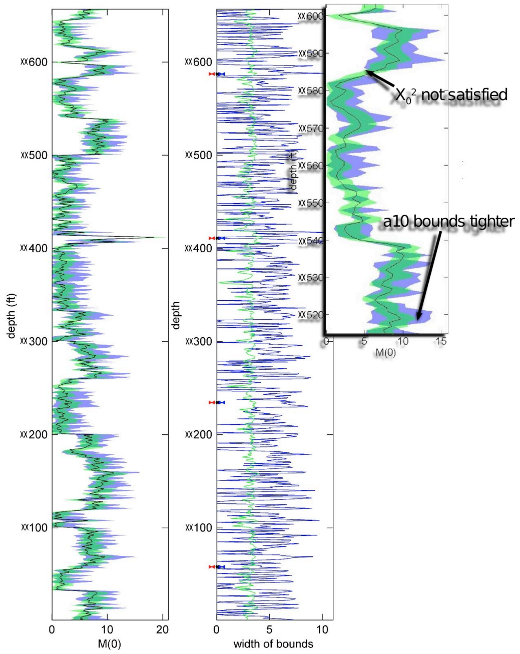
Abstract:
Calculation of uncertainties from the Laplace inversion of NMR data used in the determination of oil field rock porosity is an important and under-valued area. An improved technique for calculating the uncertainty of NMR data has been developed. This method, denoted as A_{10} uses a constraint based on the means of the first 10 echoes in addition to the χ^2 constraint used in the Parker et. al. method [4,5]. The Parker method is sensitive to the characterization of noise in the raw data and as a result the bounds can vary significantly. This new method produces much tighter, more realistic values for the porosity bounds. Using advanced processing algorithms and multi level processing platforms, we were able to reduce the calculation time down to minutes.



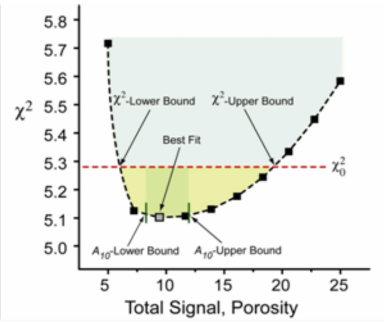


Figure-2: Parker's model: plot of bounds on porosity for a given depth = 3150 ft. In this pot χ^2 = variance of (data - fit) and χ_0^2 is obtained from the experimental noise variance

Figure-1: Left panel: The upper and lower bounds of rock porosities using A_{10} (green) and original Parker (blue) method. Right Panel: The relative widths of the ranges as determined by both methods. The inset highlights the differences between the methods.

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Numerical modeling of the carbonate and the sandstone formations

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It is of critical interest in the well-logging to make a reliable estimation of permeability of the formation via more accessible properties such as the length scale derived from NMR response. When the pore geometry is simple (quasi-periodic glass bead packs or clean sandstones), there are working empirical models that correlate the porosity and the length scale to the permeability. For heterogeneous carbonate rocks, such laws, based essentially on the notion of tortuous pipes of an effective hydraulic diameter and simplified interpretation of the NMR data, fail to give a consistent prediction and require an ad-hoc modification specific to the formation. The presence of ramified channels of varying capacity in these systems brings in a transport behavior qualitatively distinct from that of a quasi-periodic system. Heterogeneity and diffusive coupling further undermine the validity of the MR interpretation in extracting the controlling length scale parameter. Using the parallel Lattice Boltzmann and random walk simulations, we study transport and diffusion properties in various types of pore geometry, from simple 2D micro-fluidic mazes, 3D glass-bead packs and sandstones to more complex carbonates. In this work, we focus on the distinction between the sandstones and the carbonates as manifested in the numerically observed flow profile and diffusive/relaxation properties and try to develop a sound interpretational framework for complex porous media beyond the glass bead packs and sandstones. The author would like to thank colleagues at SDR and SCR for providing me with tomograms of carbonate rocks.

Spin Dynamics Simulations of Multiple Echo Spacing Pulse Sequences in Grossly Inhomogeneous Fields

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Pulse sequences with multiple lengths of echo spacings are used in oilfield NMR logging for diffusion-based NMR applications such as rock and fluid characterization. One specific implementation is the so-called diffusion editing sequence comprising two long echo spacings followed by a standard CPMG at a shorter echo spacing[1]. The echoes in the CPMG portion contain signal from both the direct and stimulated echoes.

Modern oilfield NMR logging tools are designed for continuous depth logging of earth formations by projecting both the static (B_0) and dynamic (B_1) fields into the formation. Both B_0 and B_1 profiles are grossly inhomogeneous which results in non-steady-state behavior in the early echoes. The spin dynamics effects present a challenge for processing the echo amplitudes to measure porosity (amplitude extrapolated to zero time) and attenuations for fluid or pore size characterization.

In this work we describe a calculation of the spin dynamics of the diffusion editing sequence with two long echo spacings. Quantitative understanding of the early echoes allows for improved characterization of heavy oil, gas, and other applications. The calculation takes into account full B_1 and B_0 field maps, and comparisons will be made for sensors and parameters typical of oilfield logging tools and environments.

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A numerical analysis of NMR pore-pore exchange measurements using Xray-μCT techniques

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Pore-pore exchange experiments are a recent development[1] and hold great promise to spectrally derive length scales relevant for transport in porous media. In particular, NMR Laplace techniques like relaxation or exchange spectroscopy reach a spectral length scale resolution much higher than available from μCT images, but provide no spatial resolution. A combination of both techniques can lead to better models for regions of unresolved porosity in μCT images, implying increased accuracy for transport calculations based on such images.

In this study we carry out numerical NMR pore-pore exchange experiments on selected Xray-CT images of sandstones and carbonate rock, while at the same time tracking information about the geometry and topology of the pore space. In particular, we use random walk techniques and observe the radius of gyration for random walks in each encoding or diffusion interval as well as measuring local diffusion averaged relaxation rates in a forward modeling approach, including the effect of internal fields. Diffusion averaged internal field distributions and relaxation time distributions are in good agreement with experiment. We use pore partitioning techniques and geometric distance fields to relate the pore-pore exchange and relaxation spectra to underlying structural quantities, namely pore size, initial distance to a relaxing surface, and travelled distance. In addition to the concept of 'pores' and 'throats', e.g. convex/simple objects within the pore space connected by narrow constrictions, we use a diffusion averaged local surface to volume ratio to compare simulation data with experimental measurements.

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Relaxation-relaxation exchange experiments with portable Halbach-Magnets

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Relaxation-relaxation exchange experiments were performed on two-phase gas-liquid systems. To conduct such experiments at low field with mobile NMR under the extraction hood, new Halbach-Magnets were designed and built. One is characterized by maximum simplicity, the other by an improved homogeneous magnetic field and a maximum accessible sensitive volume. The construction of the magnets and their performance are described and the results of first experiments are reported. We anticipate that this and related 2D NMR experiments will be of great use to monitor multi-phase reactions on line.

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Non-invasive NMR profiling of painting layers

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Restoration and conservation of paintings requires in-depth knowledge of the materials used, their properties as function of time, the environmental exposure and the distribution of materials in artwork. As moving paintings for analysis is connected with great effort or not possible at all, it is advantageous to move non-invasive diagnostic equipment to the paintings. Common non-invasive methods of analysis are restricted to surface layers, and lower layers cannot be accessed non-destructively. This is why we investigated the use of single-sided NMR sensors as an alternative method. With the Profile NMR-MOUSE, deeper layers can be accessed non-invasively to collect information about the stratigraphy of paintings and their support.
This work reports results obtained by the Profile NMR-MOUSE. Binder aging and the thickness of proton-rich layers in paintings were characterized in situ without contact to the surface. The suitability and accuracy of this method were tested on two easel painting models consisting of copper acetate and cobalt blue in comparison to optical and electron microscopy. Depth profiles were measured that revealed amplitude variations consistent with the different layers of the paintings. The accuracy of thickness values determined non-destructively by NMR was conformed by destructive optical microscopy of painting models to be of the order of 20 μm. Different Italian Renaissance paintings were analyzed by the NMR-MOUSE in the National Gallery of Umbria in Perugia. My measuring NMR depth profiles at contingent spots of a painting, it is possible to build a 3D map of the statigraphy. Furthermore, the nature of the binder and its aging characteristics can be studied by their T_1 and T_2 relaxation signature. Artificially aged and naturally aged tempera binders can at least in the cases studied be differentiated. This makes it possible to identify recently restored sections in a painting and raises the hope to potentially identify forged tempera paintings.

Single-shot depth profiling with a single-sided NMR sensor: application to skin measurements

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Portable open NMR probes built from permanent magnets like the NMR-MOUSE offer several advantages over conventional NMR systems. They are small in size, low in cost and robust. However, associated with the open geometry of the magnets are a number of challenging limitations. The strong stray field gradient of such sensors limits the thickness of the sensitive slice to be much below one millimeter, imposing an important restriction to the experimental time required to profile large depth ranges into the sample [1]. In this work we exploit the concept of field shimming by means of a shim unit based on permanent magnet blocks [2] to strongly reduce the magnetic field gradient along the depth direction while keeping the lateral components under control. Under these conditions depth profiles over a range of some millimeters can be measured with a resolution of 50 µm in a single-shot as the Fourier transform of the echo signal acquired in the presence of a static gradient of about 1 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 proper design of the shim unit, the reduction in the static gradient is not achieved at expenses of a strong reduction in the magnitude of the average field, a price usually paid in conventional designs. The field of the first prototype is about 0.3 T, which is comparable to the field generated by a previous sensor of the same size [3].

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Magnetic Field Gradient Monitor (MFGM)

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Porous media are of considerable interest in a very diverse range of activities. Pore diameters range from subnanometer to macroscopic dimensions. Frequently their use or importance is intimately connected with their transport properties. Diffusion and flow measurements in porous systems are therefore of practical relevance.

Pulsed-field-gradient NMR (PFG NMR) has proven valuable for the study of both diffusive and coherent molecular motions. Accurate PFG NMR studies of motions of large molecules are, however, at present still difficult. For large, slowly moving species the required gradient pulses must have large amplitudes, and the resulting eddy current fields can cause errors in the phase encoding [1-2]. Restricted diffusion of smaller molecules in porous media encounters similar difficulties.

Despite continued advances in NMR hardware, imperfections in the magnetic field evolution during measurements still hamper numerous MR procedures. Large and fast gradient switching provokes undesired dynamic field perturbations by various mechanisms such as eddy currents, limited gradient bandwidth or heating effects. Reproducible field perturbations can be determined approximately by existing measurements [3-5].

In this work we will present a novel method, related to but significantly different from our previous methods [6]. We will compare our new method to other recent advances in magnetic field gradient waveform/k-space trajectory measurement. Our new method significantly improves applications, which either require high gradient waveform fidelity and/or suffer from eddy current distortions (i.e. diffusion, flow, and phase contrast imaging).

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Compositional analysis of materials with unilateral NMR

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We were interested in developing experimental protocols that enable the discrimination between different sorts of liquid (e.g. oil and water) on the basis of their molecular mobility, using unilateral (open-access) magnets. Because of the field inhomogeneity inherent to unilateral magnets, our study was bounded by spin echo experiments, particularly by those based on the Carr-Purcell-Meiboom-Gill (CPMG) sequence. Here we present two ways to utilize CPMG for our purpose. First is to employ a difference in relaxation times (T_2) of the constituents, which is manifested in a multi-exponential decay of a CPMG signal. To know how much of each T_2 component is present in the signal, we performed a multivariate regression of the decays, using a classical least-square algorithm. A performance of the method is demonstrated on model food samples, made of water and cod oil mixture stabilized by agar, as well as on a series of bitumen sands. The prediction accuracy is strongly dependent of whether the calibration samples had characteristic T_2 similar to those in the test samples. Thereby, a proper choice of calibration samples is the main factor of accuracy.

The second way is to perform a diffusion-weighted CPMG experiment, where constituents are discriminated through a difference in their diffusivity rather than T_2. The diffusion delay that is needed for efficient suppression of a ‘faster’ constituent (water) depends on the magnetic field gradient, hence the method includes a respective calibration procedure. Once an appropriate diffusion delay is found, the amount of a ‘slow’ constituent is proportional to the CPMG amplitude. This method is insensible to the T_2 variation over the samples, as we demonstrate here on example of commercial beef samples, but requires for slower and faster diffusing components to have comparable T_2.

Design methodology of a unilateral NMR apparatus

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Unilateral NMR apparatus using a barrel magnet, which was originally introduced by Fukushima and Jackson [1], was found to be useful for investigating away from the apparatus due to the large sample volume [2]. However, it was pointed out that there is a non-negligible contribution from the regions with large magnetic field gradients. This problem is similar to the one already known for the CMR (Combinable Magnetic Resonance) by Schlumberger [3]. In the presence of magnetic field gradients, diffusive motion leads to a signal decay that will augment the normal T_2 decay. Due to the complex pattern of the field gradients of the barrel magnet, it is not straightforward to extract the intrinsic T_2 value. Therefore, it is desired to reduce the contribution from such regions.

Local sensitivity is defined by B_0 and B_1 distributions, both of which show complex patterns on a unilateral NMR apparatus. Thus, it is not straightforward to obtain the optimum setup just by improving the homogeneity of one of the magnetic fields. Therefore, we try to accomplish our goal by using a sensitivity map for evaluation. The voltage induced in the coil from a uniform sample in grossly inhomogeneous fields can be written as [3]

$$V_{x,y}(t) \propto \int \left[B_0^{\,2}(r) \frac{\omega_1(r)}{I} F(\Delta\omega_0(r)) m_{x,y}(r,t) \right] dr . \qquad (1)$$

Here, $F(\Delta\omega_0)$ is the frequency response of the detection system, including the coil response and any hardware or software filters. The quantity $m_{x,y}(r, t)$ is the transverse magnetization at point r and time t, which depends on both hardware properties and pulse sequence. Figure 1 shows a sensitivity map calculated for the current apparatus with a barrel magnet and double-D shaped rf coil. Radially extending lines correspond to the regions with large field gradients.

In order to obtain a coil design that only excites the region with a small field gradient, $\Delta\omega_0$ distribution weighted by sensitivity at each point was calculated from Eq. (1) with changing the position and length of the straight wires composing a double-D coil. Figure 2 shows a sensitivity map with improved $\Delta\omega_0$ distribution, which was obtained as a result of brute-force procedure in a relatively small search space. By using an appropriate optimization algorithm, it is expected to extend the search space that may lead to a better solution.

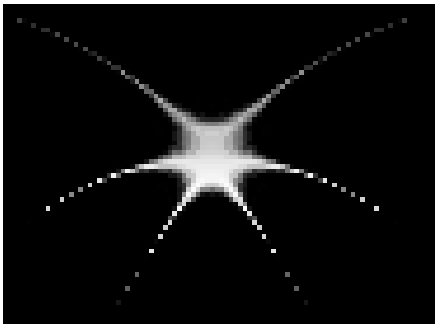

Fig. 1. Sensitivity map for the current apparatus. Surface of the apparatus is located at the bottom of the figure. Radially extending legs correspond to the regions with large field gradients.

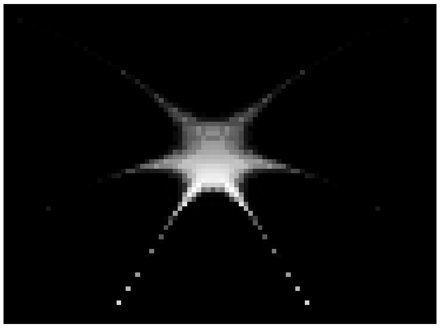

Fig. 2. Sensitivity map for the new coil design. Contribution from the radially extending legs is reduced from Fig. 1.

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Strategies and New Technologies for Improved Production of Hyperpolarized ^{3}He and ^{129}Xe

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NMR and MRI with hyperpolarized noble gases have a myriad of applications in medicine and material science, including porous and granular media. In our experiments, nuclear-spin polarized ^{129}Xe or ^{3}He gases are produced by optically pumped spin-exchange with Rb atoms. Signal-to-noise efficiency is generally limited by either low polarization or slow production rates. One key technical problem in optimizing ^{129}Xe or ^{3}He polarization levels is the amount of obtainable resonant laser light from the current generation of Laser Diode Arrays (LDA), which have broad optical spectra (see Fig.1). A recent solution has been the development of Volume Holographic Gratings (VHG) that self-seed the laser to provide a tunable narrow resonant line output with only minimal laser power reduction [1]. We have recently employed novel, prototype-commercial VHG-narrowed lasers for spin-exchange optical pumping of noble gases for the first time [2].

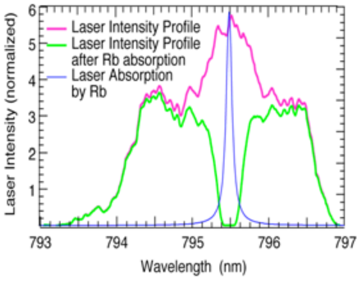

***Fig 1*:** Laser line-shape from a typical LDA. The pink line is the measured LDA output; the green line is the laser spectrum after traversing the optical pumping cell. The blue line is the calculated absorption by Rb during ^{129}Xe spin exchange.

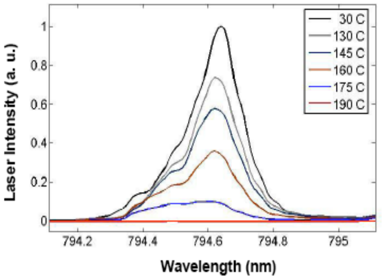

***Fig 2*:** Laser line-shape from a commercial VHG-line-narrowed 30W laser. The spectra were taken after the light has traversed the ^{3}He optical pumping cell. Notice that the line-width of the laser is ~ 0.2 nm and all the laser power is absorbed when the cell temperature is at 190°C.

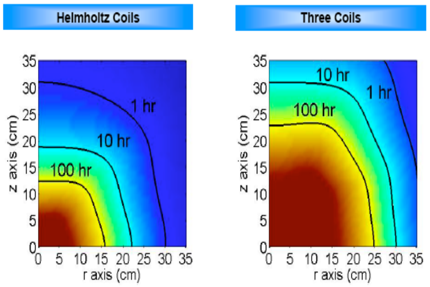

***Fig 3*:** Simulated magnetic field plots, and contours showing the calculated ^{3}He T_1 due to diffusion in field gradients. The Helmholtz pair previously used to provide the holding field for optical pumping (left), and the modified three-coil design (right).

For hyperpolarized ^{3}He in particular, the time required to polarize a suitable volume of gas (~ 15-20 hours for ~ 0.5 L) has also been a major obstacle. To address this problem, we have designed four storage cells to hold the hyperpolarized ^{3}He gas in our system for 30-40 hours with minimal polarization loss. This design required a much more homogeneous magnetic field region than had been used for optical pumping alone. Adding another coil at the center of the polarizer, in addition to the previous Helmholtz pair, has increased the working volume by a factor of 6 as shown in Fig. 3 [3]. The storage cells will then be coupled with a switch to Rb/K hybrid spin-exchange [4], which can enhance ^{3}He production rates by a factor of 4.

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Low cost CE-NMR with microcoils for chemical detection

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Understanding speciation in solids and solutions is important for environmental and toxicological purposes. Capillary electrophoresis (CE) is a simple rapid separation method that can be used to identify species in solution. One of the challenges with CE is obtaining a method of direct detection that can provide speciation information. Nuclear magnetic resonance (NMR) has been used to identify chemical species in aqueous solutions and has also been coupled to CE. We are developing separation protocols to determine the speciation of chemical complexes in solutions with minimal perturbation to the original sample equilibrium. On-line NMR measurements will be made downstream of the UV detector. We will discuss our development of a low-cost microcoil CE-NMR system for in situ characterization of samples of interest.

Prepared by LLNL under Contract DE-AC52-07NA27344.

A new spin exchange optical pumping (SEOP) modality for hyperpolarized ^{129}Xe production and use in porous media

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Recent studies using hyperpolarized ^{129}Xe as the fluidizing gas to probe exchange measurements in this system were subject to extreme temporal averaging due to the very low ^{129}Xe polarization – see Fig. 1 [1]. The requirements of a continuous flow of hyperpolarized ^{129}Xe and that it not be diluted with another gas of high diffusivity severely limits the polarization that can be achieved by conventional continuous flow spin exchange optical pumping (SEOP). The low polarization is a combination of short residence time of the xenon in the optical pumping cell and the high partial fraction of xenon leading to higher electronic Rubidium spin destruction. In an attempt to improve SEOP efficiency and thus xenon polarization we used a frequency narrowed laser based on Volume Bragg Grating (VBG) techniques developed by our team [2]. Preliminary results in a continuous flow cell using a 90% Xe, 10% Nitrogen mix showed a tripling of polarization levels compared to pumping with a conventional broad-band laser diode source [3]. Best ^{129}Xe polarization was achieved with the narrowed laser pumping on the wings of the Rb absorption profile [3]. Further investigation of pumping with a VBG laser both in continuous flow and stop-flow modalities has lead to the discovery that the achievable ^{129}Xe polarization is sensitive to the interdependence of the optimal cell temperature and the Xe density [4]. We report here for the first time record high levels of ^{129}Xe polarization at high partial fraction of xenon within the SEOP cell – see Fig. 2. The levels achievable will have profound impact on experiments in porous and granular media allowing non-averaged single shot NMR spectra to be recorded. This method will also enable stop-flow production for ^{129}Xe clinical lung MRI [4].

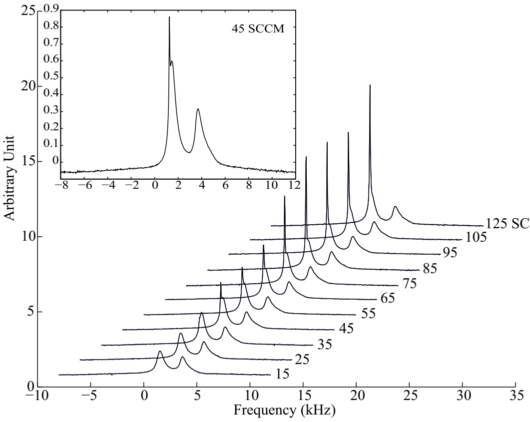

Fig. 1: Plot of Xe spectra for range of flow rates through the bed. Inset is for case of 45 SCCM

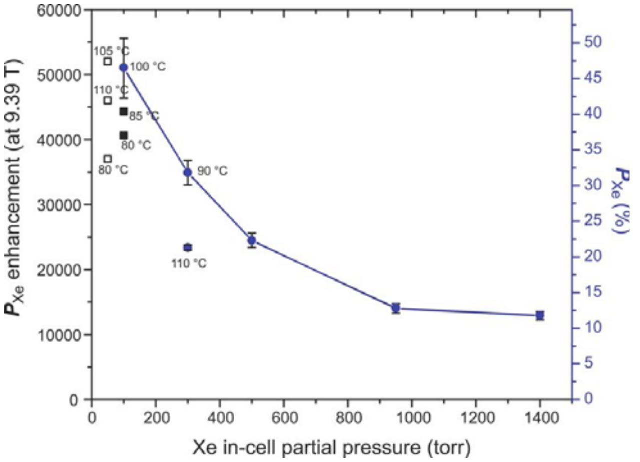

Fig. 2: Xenon polarization as a function of cell temperature and partial fraction of xenon within a 2000 Torr mix. Balance of mix is Nitrogen. All results were taken with a 30W VBG laser module.

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