Emerging Applications of NMR Logging in Groundwater Monitoring and Environmental Remediation

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SUMMARY

New applications of NMR logging tools in groundwater and environmental applications have been developed and demonstrated. Long-term in-situ measurements with NMR logging tools were used to detect and monitor biofouling and biogeochemical changes in aquifers on measurement scales ranging from days to years. NMR logging measurements in flowing or pumping wells were shown to be sensitive to the distribution of groundwater flow velocities in adjacent unconsolidated aquifers. NMR diffusion measurements with an NMR logging tool were shown to be capable of separating and measuring the bulk fluid concentrations of water and diesel fuel with different fluid fractions saturating a natural medium to coarse sand.

Key words: NMR Logging, Nuclear Magnetic Resonance, Groundwater Remediation, Aquifer Characterization, NAPL.

INTRODUCTION

NMR logging has been used for decades in petroleum exploration, with primary applications to measure porosity, estimate pore size distributions and permeability, and estimate the fluid fractions and viscosities of water, oil and gas in earth formations (Kenyon et al. 1995). More recently, small-diameter NMR logging tools have been developed specifically for groundwater and environmental applications (Walsh et al. 2013), and these tools have been widely used to estimate aquifer properties including total, bound and mobile porosity, hydraulic conductivity and unsaturated water content at vertical resolutions of 0.5m. Here we present the initial development and experimental results of three specialized applications of NMR logging relevant to high resolution aquifer characterization and contaminant remediation.

NMR logging was applied to monitor pore-scale changes related to bio-remediation processes, on time scales ranging from days to years. NMR logging measurements are potentially sensitive to many pore-scale biogeochemical processes related to active or natural remediation of contaminants, including the growth of biofilms, the generation of mineral precipitates, and the oxidation and/or reduction of iron and other magnetic minerals. The primary benefit of using NMR logging for monitoring such processes is that NMR can measure these processes as they unfold within the undisturbed native formation. NMR monitoring can also potentially reduce the manual labor, drilling, material handling and disposal costs associated with drilling and sampling programs. Short-term stationary and repeat-logging NMR measurements, performed in the laboratory and the field, clearly demonstrated the ability to detect and characterize the growth of biofilms in permeable saturated sediments, on time scales of days and weeks. Longer-term stationary and repeat-logging NMR measurements were performed to monitor pore-scale changes related to natural and stimulated bioremediation of uranium over time scales on the order of 1 year. These experiments yielded unclear or null results (i.e. no detection of any significant change) while demonstrating the long term stability of the instrumentation.

NMR logging measurements were applied to estimate the flow velocity distributions and the fraction of pore water that actually participates in groundwater flow. The distribution of groundwater flow velocities in a contaminated aquifer can have a major impact on the spatial distribution of groundwater contaminants over time, and this can impact contaminant plume prediction and remediation strategies. NMR logging measurements were applied in screened sections of monitoring wells under pumping and non-pumping conditions in two vertically separated permeable aquifers. The NMR measurements indicated that although the two aquifers had similar total porosity and pore size distributions, the upper aquifer exhibited approximately uniform flow velocity among the majority of large pores, while the lower aquifer exhibited high flow velocity for a minor portion of the large pore water and low flow velocity for a major portion of the pore water.

NMR logging diffusion measurements and 2D inversion methods (T2-D) were applied to directly detect and measure bulk non-aqueous phase liquid (NAPL) contaminants in permeable aquifers. The ability to directly detect, measure and characterize the state of bulk NAPL contaminants within undisturbed contaminated formations is a critical objective in many groundwater remediation projects, and at present there are few available or cost-effective means for meeting this objective. NMR logging diffusion measurements have been recently suggested as a means to directly detect and measure bulk NAPL concentrations in formations adjacent to monitoring well bores. NMR logging diffusion measurements were performed in the laboratory, on various mixtures of water and diesel fuel saturating sand, using a diffusion-editing pulse sequence and 2D T2-D NMR inversion methods. The results show that existing small diameter NMR logging tools are capable of directly detecting and accurately estimating the fluid fractions of water and diesel in medium-coarse sand.

METHOD AND RESULTS

NMR Monitoring of Biofouling Processes in Formation

We performed laboratory and field experiments to demonstrate the use of an NMR logging tool to detect and monitor the growth and evolution of biofilms and biofouling in engineered and natural saturated sediments. Initial demonstration was performed at the Montana State University using a 3.5 inch diameter Javelin NMR logging tool in a specially-designed bioreactor, shown in Figure 1. The lab-scale bio-reactor was constructed inside the Faraday cage and wet-filled with 1mm nominal quartz sand. The system was sterilized, and an initial round of experiments was conducted with the Javelin to obtain baseline measurements of the system when saturated with sterile buffer solution. The reactor was then inoculated on Day 1 with an effluent containing biofilm forming bacteria, which was the fed over the course of days with nutrient while NMR monitoring data were acquired. Experiments were conducted with the Javelin device during the pumping of the inoculum and immediately following during the no-flow bacterial attachment phase. Between Days 2—7, a series of eight experiments were conducted daily with the Javelin to monitor parameters changing within the reactor due to biofouling.

Figure 1. NMR logging tool and bioreactor used for initial demonstration of detection and monitoring of biofouling.

This experiment demonstrated that the Javelin tool can detect small to moderate changes in T_2 distribution due to environmentally relevant quantities of biofilm in quartz sand. In general, the data showed no significant effects from flow or diffusion. The experimental data in Figure 2 indicate a shift in the T_2 distribution over the course of 2 days to faster decay times, indicating that the fluid properties and pore environment changed due to biofouling. The graphs below show the sum of echoes (DOE) statistic, which is a highly stable indicator of mean T2 and/or saturated porosity.

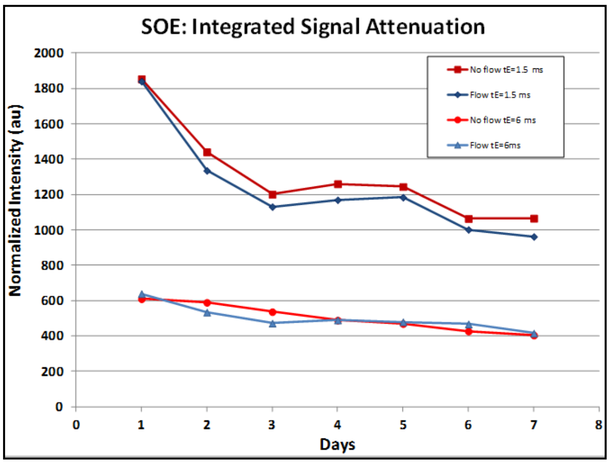

Figure 2. The normalized Sum of Echoes (SOE) indicates that the mean value of the T_2 decay decreased over the course of the experiment by approximately 40% overall and 27% between Day 2 and Day 7, due to growth of biofilm within the saturated sand pack.

Follow-up field-scale experiments were conducted at a bioremediation research site near Butte, Montana USA. Two 3.5 inch diameter NMR logging probes tuned to different frequency ranges were deployed in screened intervals of two PVC-cased monitoring wells. NMR monitoring data were acquired using a new multi-channel/multi-frequency NMR logging system. Measurements were conducted over a 17-day period, beginning with a background bleach and high-flow flush to remove any pre-existing biofilm from the saturated and unconsolidated (mostly sand) formation in the immediate vicinity of each well. Molasses-based nutrient was then injected using tubing installed along the outside of the probes to stimulate biofilm growth. Hosing was also installed along the axis of the probe to induce radial flow that might be measured during the experiment. The NMR results showed a very pronounced shift in the T_2 distribution from long to short times from the time of bleaching and inoculation to Day 10 when biofilm growth reached a peak. The time series of the NMR decay time clearly reflected a rapid onset of biofilm growth starting 3 days after the inoculation.

Long-term NMR Monitoring of Bioremediation in Iron-Rich Aquifers

A second program of laboratory and logging NMR experiments was performed to investigate the ability to monitor changes in sediment iron mineneralogy due to temporal changes in groundwater chemistry. Certain changes in groundwater chemistry, and specifically changes in groundwater redox conditions, have been shown to cause transformation and immobilization of uranium and other heavy metal contaminants. These geochemical reactions are often linked to changes in iron mineralogy, which could potentially be detected via NMR as changes in T2 relaxation and/or diffusion relaxation. A series of bench-scale laboratory NMR experiments were designed to mimic a cycle of geochemical changes expected to occur at the Rifle Colorado Integrated Field Research Challenge site. The bench-scale NMR experiments demonstrated the ability of low-field (~280 kHz) NMR measurements to detect and monitor changes in iron minearalogy under both reducing and oxidizing changes. The laboratory experiments also indicated that it is easier for

NMR to detect such changes when the initial NMR signal relaxation is relatively long (i.e. in relatively large pore sizes).

A parallel field experiment was performed using two NMR logging tools installed in boreholes at the Rifle Colorado site. One probe was left in place for a continuous period of 15 months to monitor the NMR response through two consecutive annual runoff cycles. The NMR monitoring measurements shown in Figure 3 indicated a possible decrease in NMR relaxation during the first runoff cycle – which was the anticipated result based on recent aquifer amendments and groundwater flow and chemistry patterns at the site. The monitoring measurements did not indicate a significant change in NMR response through the second runoff cycle.

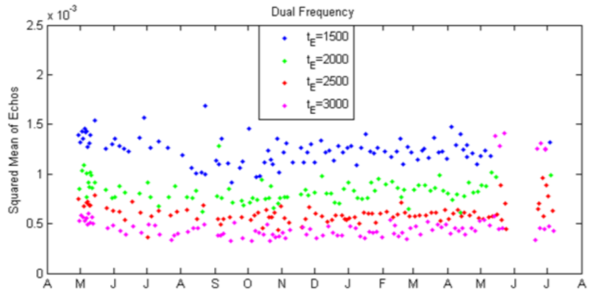

Figure 3. The complete 15-month time series from well 6D displaying the trend of NMR squared mean of echoes over time.

NMR Measurement of Flow Velocity in Formation

Another objective of this research was to develop and demonstrate a logging NMR-based method of measuring the flow velocity distribution in an unconsolidated aquifer. We developed and investigated two NMR flow measurement methods that exploit the design of the Javelin NMR logging tool, which produces a very thin roughly cylindrical sensitive zone surrounding the tool, and a large static field gradient that drops off with radial distance from the tool.

The difference between the CMPG time decay curves under non-flowing and flowing conditions provides a simple and direct estimate of the volume of water that has left the NMR sensitive zone at any time after the excitation pulse. For example, in Figure 4, at t = 200ms, the T2 decay curve with no-flow has an amplitude of 21.8%, and the T2 decay curve under flowing conditions has an amplitude of 13.5%. Thus, we can estimate that a volume of water equivalent to 8.3% porosity has exited the NMR sensitive zone in a time span of 200 ms.

A second independent measure of flow can be obtained by comparing the initial amplitudes of the T2 curves, under flowing and non-flowing conditions, following the application of a pre-saturation pulse and T1 recovery delay. The pre-saturation pulse resets the NMR magnetization in the NMR sensitive zone to zero. Under non-flowing conditions, T1 relaxation occurs during the delay between the pre-saturation pulse and start of the CPMG sequence, and this magnetization is measured at the initial amplitude of the resulting CPMG decay curve. Under flowing conditions, any water that remains in the NMR sensitive zone also experiences this T1 recovery, but new water also flows into the NMR sensitive zone during this delay, and this additional new water adds to the initial amplitude of the resulting CPMG decay curve. Thus, the difference between the initial amplitudes of the T2 decay curves, under flowing and non-flowing conditions, provides a direct estimate of the volume of water that has entered the NMR sensitive zone during the time delay between the pre-saturation pulse and the start of the CPMG sequence.

NMR measurements of flow in native aquifer formations were performed in two 4-inch diameter PVC monitoring wells in Larned Kansas USA, in May 2013. NMR measurements were performed with a 3.5 inch diameter Javelin NMR logging probe, with the tool positioned in the center of each 5 foot screened section. Well LEC2 was screened in the semi-consolidated High Plains aquifer, at a depth of around 20 meters. Well LEA3 was screened in the alluvial aquifer at a depth of around 8 meters. CPMG measurements were performed under flowing and non-flowing conditions. Additional measurements were performed using a pre-saturation pulse, followed by a variable waiting time between 100ms and 800ms, followed by CPMG sequence. The pre-saturation experiments were also performed under both flowing and non-flowing conditions. The flow for all flowing measurements was induced by siphoning water from a water tank at the surface in to the top of each well. A flow control valve was used to maintain a nearly constant flow rate of approximately 20 gallons per minute.

Figure 4 shows the fitted T2 water content distributions in Well LEC2 (High Plains aquifer), under flowing and non-flowing conditions, and also with and without the application of a pre-saturation pulse and 200 ms T1 recovery delay. For example, at t = 200 ms, the T2 decay curve with no-flow has an amplitude of 21.8%, and the T2 decay curve under flowing conditions has an amplitude of 13.5%. Thus, we can estimate that a volume of water equivalent to 8.3% porosity has exited the NMR sensitive zone in a time span of only 200 ms. At 400 ms, the difference between the T2 decay curves is equivalent to a porosity of 10.2%. Analysis of these curves indicate that in this portion of the high plains aquifer, less than half of the pore water is moving at a relatively high velocity and entering/exiting the NMR sensitive zone in less than 200 ms.

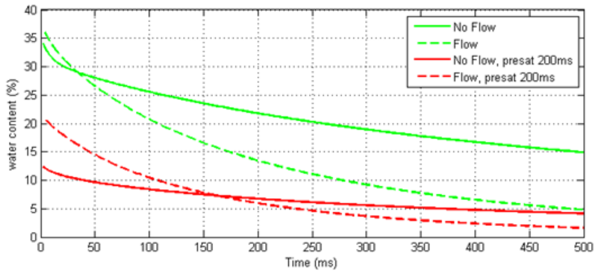

Figure 4. Larned Well LEC2 (High Plains aquifer). Fitted CPMG decay curves under flowing and non-flowing conditions indicate less than half of the pore water is participating in fast flow, with most of the water experience low or no flow.

Figure 5 shows the fitted T2 water content distributions in Well LEA3 (alluvial aquifer), under flowing and non-flowing conditions, and also with and without the application of a pre-saturation pulse and 200 ms T1 recovery delay. Compared to the T2 decay curves from LEC2 (Figure 4), there is less overall difference between the T2 curves in flowing and non-flowing conditions, which indicates that the water in the NMR sensitive zone is not being replaced as quickly, even at the same well flow rate of 20 gal/min, as in LEC2. Also, the difference in the initial amplitudes of the decay curves in the flowing and non-flowing conditions, following pre-saturation and a time delay, is much lower in LEA3 than LEC2. This also indicates that more water is participating in the flow, and the velocity of "new" water moving into NMR sensitive zone is slower the alluvial aquifer than in the High Plains aquifer.

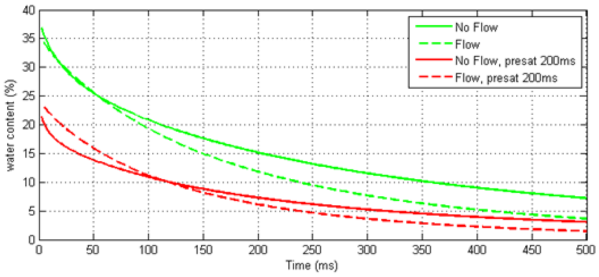

Figure 5. Larned Well LEA3 (alluvial aquifer). Fitted CPMG decay curves under flowing and non-flowing conditions indicate that flow velocity is more uniform and slower than in the high plains aquifer.

NMR Detection and Measurement of NAPL in Formation

Non-invasive detection, localization and measurement of bulk NAPL contaminants in unconsolidated aquifer sediments remains a difficult and largely unsolved problem. We performed laboratory NMR measurements to demonstrate the feasibility of using a commercially-available NMR logging tool to unambiguously detect and measure the volume fraction of bulk diesel fuel mixed with water in medium to coarse sand.

The NMR measurements were performed using a Dart NMR logging tool, and diffusion-editing pulse sequence. The Dart tool has a diameter of 1.75 inches, operates at frequencies of 425 kHz and 475 kHz, has an NMR sensitive zone at a radius of about 3 inches from the center of the tool, and a magnetic field gradient of approximately 30G/cm within the NMR sensitive zone. The pulse sequence used static gradient diffusion editing, with a CPMG echo spacing of 500 us and a variable diffusion editing delay between 500 us and 12,500 us. Samples consisted of variable mixtures of water and diesel saturating medium-coarse Ottawa sand, prepared in 5 gallon plastic buckets. The NMR logging tool was lowered into a 2 inch inside diameter PVC access tube, which was positioned in the center of each sample. Recorded NMR data were processed using a 2D inverse Laplace transform to isolate the contribution of different NMR-detected fluids in a 2D space of T2 relaxation and Diffusion relaxation.

Figure 6 shows the resulting T2/D distributions of sand saturated with a) water only, b) 60% water and 40% diesel, and c) diesel only. These 2D inversion results show clear separation and discrimination of the water and diesel fractions, with greatest contrast in the measured NMR diffusion rates of the two fluids. The volume fractions of water and NAPL for these three results can be estimated by applying a threshold at $Log_{10}(D)$ ~ -9, and integrating the 2D NMR signal distributions above this line for water and below this line for NAPL.

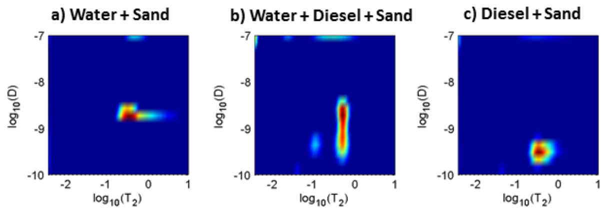

Figure 6. 2D inversion of Dart NMR data acquired using static gradient diffusion editing pulse sequence shows clear separation of NMR signals from water and diesel.

CONCLUSIONS

This compilation of recent research has shown that small diameter NMR logging tools have potential uses in characterization of aquifers and groundwater remediation beyond the traditional uses in measuring water content and estimating permeability. Medium-term and long-term in-situ NMR monitoring has been demonstrated, and the ability of such measurements to detect and monitor biofouling and changes in iron redox conditions has also been demonstrated in the field. NMR logging measurements are sensitive to induced flow within the native formation, and the resulting NMR data can shed light on the nature of flow within unconsolidated aquifers. NMR logging diffusion measurements have been shown to be capable of separately measuring the volume fractions of water and diesel in a medium-coarse sand mixture.

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