

A REVIEW OF 60 YEARS OF NMR WETTABILITY

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This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Trondheim, Norway, 27-30 August 2018

ABSTRACT

Wettability is a key parameter in the development of an oilfield as it strongly affects oil saturations, capillary pressures, electrical properties, relative permeabilities and oil recovery. Despite attempts have been made to evaluate wettability downhole, the standard methods to quantify it are still laboratory based; the two most commonly used are Amott-Harvey (AH) and U.S. Bureau of Mines (USBM). These techniques are expensive and very time consuming, requiring a sample to be retrieved from the well and analysed in the lab. In several cases, the results are obtained late and only after several decisions regarding the reservoirs had to be made, without this important piece of information.

It is ubiquitously recognised that Nuclear Magnetic Resonance (NMR) is very sensitive to the strength of the fluid-rock interactions, and therefore has been considered as a good candidate for wettability determination since the '50s. The NMR signal, however, is also sensitive to several other fluid and rock properties, for example viscosity and pore size distribution, making the practical extraction of wettability information from NMR data not straightforward. NMR has, however, two considerable advantages compared to AH and USBM: it is much faster, allowing much faster turnaround of laboratory measurements, and can be measured *in-situ* downhole, with the result of the measurement being available in real time. These extreme advantages fuelled the research on the topic of NMR wettability despite the above-mentioned difficulties.

There are at least three main NMR parameters measurable downhole: T_1 , T_2 and Diffusion; with additional information extractable from the correlation between these three. Wettability affects all of these parameters, and the correlation between them. This means that there is not a single way to extract wettability information from NMR data, but there are different options.

Here, we review 60 years of literature on the topic of NMR and wettability, from the first experimental observations in the 50's to the most recent advancement. Also, this work aims at presenting strength and limitations of the techniques being developed nowadays, to help the audience make the best choice for each specific case. In this paper we focus

mostly on the lab applications, while we focused more on the downhole applications in another recent paper [1].

INTRODUCTION

Wettability is a key parameter for a reservoir, it strongly affects residual oil saturations, imbibition capillary pressure curve, electrical properties, relative permeabilities and oil recovery. The knowledge of wettability is crucial to correctly interpret petrophysical properties, to correctly model the reservoir, and ultimately to make reservoir management decision which can make the difference between success or failure of a reservoir [2].

The definition of wettability in principle is simple: "*the ability of a liquid to maintain contact with a solid surface in the presence of a third phase*". This is a simple and correct definition. However, it is totally qualitative. In fact, where the complexity arises, is on the quantification and measurement of this property. For extremely simple and perfect geometries, as a capillary tube or a smooth and flat solid surface, the contact angle can be defined. This angle is an extremely good and fundamental quantification of the wetting properties of the surface. Still, geometrical imperfection and roughness of the surface may cause the measurement to be uncertain in practice. In the case of complex microscopic geometry, or solids with multiple phases, as is the case of porous media and rocks, the contact angle becomes impractical to measure accurately, and therefore loses its reliability.

Wettability strongly affects the flow of fluids in the rock, as well as the distribution geometry and connectivity of the fluids in the rock. Because resistivity measurements are dependent on the connectivity of the fluid phases (specifically water), resistivity is also dependent on wettability. Simply described, wettability is one of several critical factors that affect the the Archie equation (1) parameter n , which represents the variation of resistivity as the saturation changes. This is equivalent to saying how the resistivity changes for different wettability values at constant saturation.

$$S_w^n = \frac{R_w}{(\varphi^m R_t)} \quad (1)$$

S_w represents the water saturation, R_w the resistivity of the water phase, φ the porosity of the rock, and R_t the resistivity of the sample. m is the cementation factor expressing how the resistivity is a function of porosity. Resistivity measurement is the oldest downhole logging technique, and still brings a lot of value, especially for its wide range of depth of investigation (DOI).

The oil industry developed robust laboratory techniques to extract meaningful wettability information from rock core plugs, such as the US Bureau of Mines (USBM) and Amott-Harvey (A-H) wettability indices. The same is not true for downhole applications, and, inferring wettability downhole is far from being a well-established answer product in the oil industry [3].

Nuclear Magnetic Resonance (NMR) is well known to be extremely sensitive to the surface interactions between fluids and solids. However, in an NMR measurement, the effects of surface interactions are always averaged with the bulk properties. For this reason, NMR becomes an effective tool for surface properties characterisation only when the Surface of interaction over the Volume of the fluid (S/V) ratio becomes big enough. This is exactly the case of porous media in general, and rocks for what concerns the oil industry. NMR is an incredibly rich technique. In general terms, it spans from high field spectroscopy for molecular characterisation of compounds (used by chemists) all the way to earth field measurements for underground aquifer, passing through relaxation analysis used for materials and food characterisation, flow and diffusion measurements and fast field cycling for molecular motion determination. Although only a minimum subset of this extreme portfolio is applicable to the landscape of oil industry, still, in petrophysics, the experimentalist has a wide choice of parameters and experiments. On one side, this freedom introduces complexity and potential pitfalls if not carefully managed, on the other end, this freedom allows to optimise the experimental setup to maximise the value in different scenarios. Most if not all the NMR experiments are sensitive to surface interactions, and therefore wettability, but in different ways. This spectrum of possibilities leads to the fact that there is not a single NMR wettability technique for which "one size fits all". Rather, there are several different techniques, and each one has its own strengths and limitation. The aim of this paper is to give the reader a flavour of this techniques developed in six decades of studies with references to the published literature.

INDUSTRY STANDARD (USBM and A-H)

The A-H imbibition and USBM tests, or a combination of both, are commonly used in the industry and widely accepted for use with core plug samples. In the A-H test, a sample at irreducible water saturation placed into a water-filled tube spontaneously imbibes water over a period of time. Then the sample is placed in a flow cell and water is forced through, with the additional oil recovery noted. The sample is now at residual oil saturation and the process is repeated with an oil-filled imbibition tube and then an oil-flooding apparatus. The result of the A-H test is given between +1 (strongly water-wetting) and -1 (strongly oil-wetting). In a USBM test, a centrifuge spins the core sample at step-wise increasing speeds starting at irreducible water saturation to residual oil saturation and then to another series of measurements. The measurement range extends from $+\infty$ (strongly water-wetting) to $-\infty$ (strongly oil-wetting), although most measurements results are in a range of +1 to -1. The centrifuge method is fast, but the saturations must be corrected because the centrifuge induces a nonlinear capillary-pressure gradient in the sample. Even though the USBM and A-H wettability indices do not always match, they are accepted in the oil industry considering there are no alternatives. These are laboratory techniques that cannot be applied downhole considering the required measurements.

NMR SENSITIVITY TO WETTABILITY

The first publications we could find that NMR relaxation for liquids is dependent on the surface to volume ratio dated back to 1956, and can be found in several articles in the Bulletin of the American Physical Society [4–6]. This initial work addresses the relaxation enhancement of the fluid on the surface layer in terms of molecular dynamics only, without discussing the solid-fluid interaction characteristic of the porous media, such as rocks. The key aspect in this work, that will be relevant for the application of NMR in porous media, is the idea of the "fast exchange regime", which happens when the diffusion across the fluid body is fast relative to the relaxation time. In this case, despite the presence of two populations of molecules with different relaxation times (one for the surface molecules and one for the bulk molecules), the measured relaxation time is a single value equal to the average of the relaxivities, weighted by the volume of molecules on the surface ($S \cdot \varepsilon$) and the volume of molecule in the bulk $V - S \cdot \varepsilon$, where S is the surface of the pore, ε the thickness of the surface layer affected by the enhancement of relaxation, and V the total volume of the pore:

$$\frac{1}{T_{2,obs}} = \left(\frac{V - S\varepsilon}{V} \right) \frac{1}{T_{2,bulk}} + \left(\frac{S\varepsilon}{V} \right) \frac{1}{T_{2,surf}} \approx \frac{1}{T_{2,bulk}} + \frac{S}{V} \varepsilon \frac{1}{T_{2,surf}} \quad (2)$$

Strictly speaking, the volume of the molecule in the bulk is $V - S \cdot \varepsilon$; however, since $V \gg S \cdot \varepsilon$, $V - S \cdot \varepsilon \approx V$. Note that equation (2) is valid for a single fluid wetting the pore surface, and there is no mention of wettability alteration or multiple fluid saturation yet.

The first report in the literature that discusses the relationship between NMR relaxation parameters and wettability is Torrey [4]. Interestingly, publications about measurement of wettability by NMR [7] appeared in the literature before the measurement of Pore Size Distribution (PSD) and microstructure properties, despite PSD being the main application nowadays. We briefly summarised the differences, advantages and disadvantages between the different NMR based wettability techniques in a previous paper [8] where we presented the T_1/T_2 ratio technique. In this review, however, we will go more into detail of each technique and focus on log applications.

T_2 BASED WETTABILITY

The first advanced wettability technique we present in this review is the one based on T_2 only. It is based on the concept presented in the previous section, but moved a long way forward since the early applications in the '50s. The main improvements of the recent techniques [9–14], compared with the early applications, is that more than a single pore size and fluid saturation, and therefore T_2 component, is considered.

$$\frac{1}{T_{2,w}} = \frac{1}{T_{2,bulk,w}} + \rho_w \frac{S_{r-w}}{V_{pore} S_w}$$

$$\frac{1}{T_{2,o}} = \frac{1}{T_{2,bulk,o}} + \rho_o \frac{S_{r-o}}{V_{pore} (1 - S_w)}$$
(3)

T_2 is determined by several parameters, and wettability is only one of the parameters, together with fluid viscosity, rock relaxivity and pore size distribution. This means that extracting reliable and quantitative wettability information from a relatively simple T_2 measurement requires several additional pieces of information. This information can only be available in the laboratory, and downhole application of this technique is usually only done on a qualitative and relative basis.

The great advantage of this technique is that allows discrimination of two conditions with the same overall wettability, but where in one case the small pores are water wet and the big pores oil wet or vice versa. Same applies for overall saturation but oil in small pores and water in big pores or vice versa. The underlying principle is to consider equation (2) as a function of pore size, where S_{r-o} is the "effective" surface of interaction between oil and rock (which is taken as proxy for pore size dependent oil wetness) and $V_{pore} S_w$ is the effective volume of water in the pore of given size (which leads to the pore size dependent saturation). The intrinsic relaxivity parameters ρ_w and ρ_o are also free parameters, but only its ratio affects the model [12].

The practical way of applying this technique (Figure 1) is to build a forward model based on the different parameters affecting T_2 , and then inverting it with a numerical method to determine the wettability and saturation functions. Aim of this paper is to give a quick overview of the different techniques, without claim of completeness, therefore we refer to the references for details, where real examples and case studies are shown.

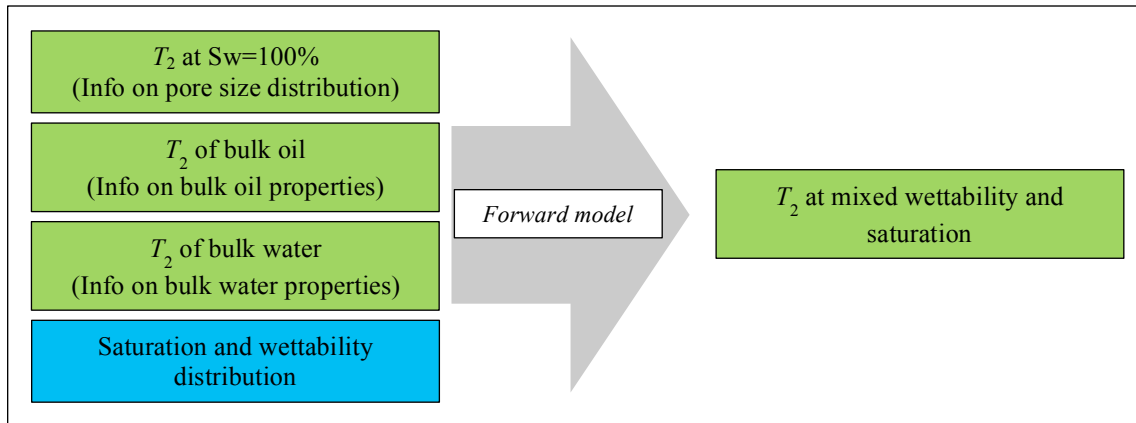


Figure 1: Forward model underlying the T_2 based wettability technique. The green boxes are measurements available (inputs) and the blue box represents the inverted data.

T_2 VERSUS SATURATION

A different way of exploiting equation (3) to extract wettability is to make measurements at different saturation states (but same wettability condition). This technique can be, in a sense, considered a simplification and derivation of the T_2 based technique. In this case, the effective fluid volume V changes with saturation, while the effective surface S does not. For a non-wetting fluid, the effective surface S is equal to zero ($S_{r-o}=0$ for 100% water wet) and therefore the second member of the addition in Equation (3) vanishes, thus making the observed T_2 of the fluid equal to the bulk value, and independent from saturation. Examples of applications of this technique can be found in the literature [15–17]. Although mostly qualitative, this technique has the potential to be applicable downhole, particularly when a tool with multiple Depths Of Investigation DOIs covering a range across the invasion profile is available.

RESTRICTED DIFFUSION

A more recent work focused on a technique applicable downhole is based on restricted diffusion [18]. Restricted diffusion for a specific fluid appears on experimental data when the size of the pore where the fluid is stored is smaller than the expected free diffusion path for the specific experimental parameters used. This means that, within some physical limitations imposed by relaxation parameters and fluid bulk diffusion coefficient, it is possible to adjust the experimental parameters to be able to see restricted diffusion for different pore sizes. The expected free diffusion path for a molecule can be predicted from viscosity (determined by salinity for water phase) and temperature. Combining the knowledge of the expected free diffusion parameter and the presence of restricted diffusion phenomena in the experimental data allows extraction of information on the true pore size, independent of relaxivity. Note that, because the expected free diffusion path increases to much more than the pore size, the information embedded in the restricted diffusion data becomes the interconnectivity of the pores or "tortuosity", which can be related to the resistivity parameter m .

The Padé [19] model combines apparent relaxivity (ρ), tortuosity (m), pore size (r) and free diffusion coefficient (D_0) to predict the relationship between T_2 relaxation time and measured diffusion (D). This appears on the D - T_2 dataset as a curved line Figure 2. From the apparent relaxivity, the wettability can be estimated [18].

$$\Delta x^2 = 2Dt_d \quad (4)$$

When a fluid is in a closed environment (as a pore in rocks), the maximum displacement is capped, and therefore is Δx^2 . This means that, increasing the diffusion time t_d over a certain value (dependent on the size of the environment) the linearity in (4) breaks. This is exactly the case called "restricted diffusion". Since maximum displacement, free diffusion coefficient and diffusion time are related, knowing two allows to determine the third. Typically, the two known parameters are t_d and D , and the information extracted

from restricted diffusion is a pore size derived from NMR data, but independent from relaxivity. Note that, when the free diffusion path is much longer than the pore size, the data become dependent to the connectivity between pores (tortuosity m), rather than the pore size.

Practically, the starting dataset for this type of analysis is a Diffusion- T_2 dataset (D - T_2) with visible effects of restricted diffusion. The data dependency along the two axes are as follow:

- Diffusion: D_0 and pore size
- T_2 : Pore size and apparent relaxivity

The free diffusion coefficient D_0 can be calculated, or at least estimated, from temperature and viscosity (for oil) or salinity (for water). The pore size dependency can be, using the Padé [19] model, eliminated to determine the apparent relaxivity and from this the wettability[18].

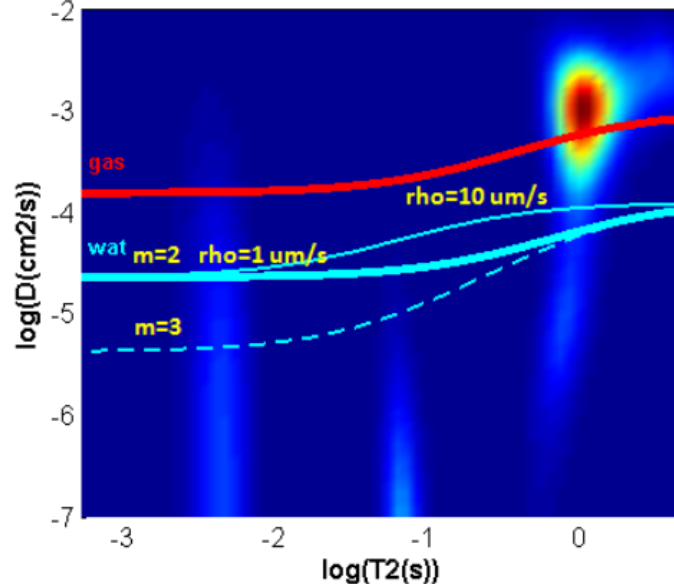


Figure 2 Dependency of the shape of the Padé line as a function of relaxivity ρ and tortuosity m (from [18])

The practical way of applying the workflow in [18] is to visually determine the location of water and oil on a D - T_2 map and fit restricted diffusion lines (Figure 2) to the fluid signals. This allows determination of the effective relaxivity of oil and water, and from this a determination of wettability (see [18] for detailed mathematical derivation).

The limitations of this technique are the following:

- it assumes uniform relaxivity across the pore spectrum.
- it assumes that we are able to measure correctly the diffusion coefficient for all relaxation times. Limitations in measuring the diffusion coefficient depends on

the technique used (pulsed field gradients or constant gradients) but there is also a dynamic limit.

T_1 FREQUENCY DISPERSION – FIELD CYCLING

There is an entire branch of NMR, called fast field cycling (FFC), NMR dispersion (NMRD), or even NMR Relaxometry, which may cause confusion with the fixed field relaxometry that is based on the measurement and interpretation of the dispersion of the relaxation time T_1 . The demanding experimental conditions for this technique make the required equipment complex and bulky and the sample size relatively small. All these conditions restrict this technique to laboratory applications and make the technique impossible to apply downhole. However, the theory connecting motion at the micro scale with NMR properties is general to any NMR application in petrophysics and porous media more generally, and therefore also useful for understanding downhole data. The theory of T_1 dispersion is useful to explain the T_1/T_2 ratio discussed below, which does have downhole applications. Further recommended literature on the theory of T_1 dispersion are [20–28].

Overall, the T_1 dispersion in frequency is an indicator of the molecular motions at the pore wall, therefore the higher the dispersion, the higher the liquid/solid interactions at the pore wall, the stronger the wetting.

If this technique is incredibly helpful to understand the physics involved in the dynamics of fluids at liquid/solid interfaces (i.e. wettability) it is quite complex to implement. Hopefully it is interesting to note that a T_1/T_2 experiment performed at a single frequency is a good proxy for the T_1 dispersion curve. It is therefore interesting to study T_1/T_2 as a proxy for wettability.

Reports on the fact that T_1/T_2 ratio depends on the effective surface relaxivity or wettability are abundant in literature. Many of the authors tie this parameter to the intrinsic properties of the surfaces, first and foremost the density of paramagnetic particles. Applications on cement [20] and rocks of different mineralogy can be found in literature [21]. Other authors refer the increased T_1/T_2 ratio to wettability effects in conventional rocks [22,23], or unconventional [24,25], where the porosity in the kerogen is expected to be strongly oil wet.

The simplest but fundamental explanation of the increased T_1/T_2 ratio for wetting fluid can be derived from studies on the phenomenon of T_1 dispersion. A detailed step by step explanation is presented in [8], here we will report only the schematic for the conceptual steps (Figure 3).

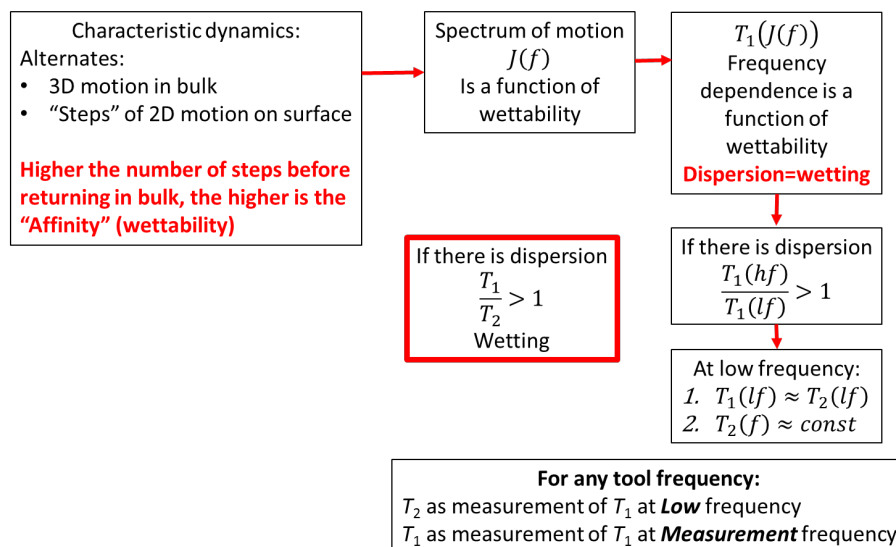


Figure 3 Schematic of the conceptual steps allowing explanation of the increased T_1/T_2 ratio for wetting fluids from T_1 dispersion data. (From [8])

T_1/T_2 RATIO

The latest technique presented discussed in this review is based on the ratio between the two relaxation parameters T_1 and T_2 . It is well established in the NMR field that both this relaxation times are determined by the characteristic molecular dynamics. The connection between dynamics and relaxation times dates back to the work by Bloembergen Purcell and Pound (BPP theory) in 1948 [29]. Briefly, for molecules with fast anisotropic motion, the two relaxation times T_1 and T_2 are equal, and therefore $T_1/T_2=1$. For a molecule with complex or slow dynamics, T_1 and T_2 become different, diverging as the motion gets slower and slower. In fact, for crystal and solid material typically T_2 extremely short and T_1 very long, several orders of magnitudes apart. Note that in NMR jargon, "fast" and "slow" is always related to the precession of the spins (Larmor frequency). Translating the description in to the time domain, which is often a more immediate visualisation, "fast" dynamics means motion for which the characteristic correlation time τ_c is much shorter than the spin precession period $T=1/f_L$ where f_L is the Larmor frequency.

In a recent paper [8], we showed with a laboratory based workflow how the oil phase T_1/T_2 ratio is strongly correlated with the industry standard USBM wettability index (Figure 4). This technique is based only on relaxation times, and not diffusion measurement. This makes the experimental part of the technique simple and robust, ideally suited for downhole applications. One drawback is that T_1 measurements are intrinsically more time consuming than T_2 since they require waiting for polarisation. Furthermore, only a single point on the T_1 recovery curve can be detected for each scan whereas several points on the T_2 decay can be acquired for each scan. T_2 is, therefore, always much better sampled, and therefore defined, then T_1 . Within this physical limit,

new NMR tools are making great progresses towards better determination of T_1 - T_2 correlation on the move.

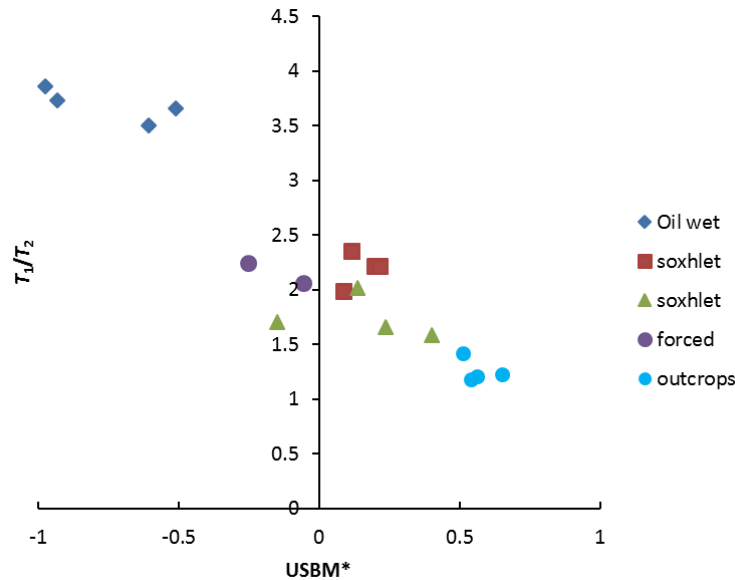


Figure 4 correlation between the average T_1/T_2 ratio for the oil phase and the measured wettability index USBM* (From [8])

The complexity into the applicability of the T_1/T_2 technique downhole is the separation of the two fluids. In fact, only one phase at the time must be analysed. Using the workflow suggested for the laboratory in [8] is not really feasible downhole for two reasons. First, doping the water phase is laborious and requires complete invasion for the entire investigated volume, which is not always verified when the formation is tight or the mud-cake build-up very effective. Secondly, the T_1/T_2 ratio for the oil may deviate from unity due to intrinsic bulk oil properties. Interpreting this deviation as due to wettability would lead to wrong conclusions. A more robust approach would be to interpret the deviation from unity of the water phase, which is expected to always have $T_1/T_2=1$ for ideal non wetting condition. Because is not possible to dope the oil phase, other "dopant-free" techniques are required to separate the fluids. A workflow based on diffusion was presented in [8]. An alternative approach can be the use of a visual recognition technique of the kind presented in [30].

CONCLUSION: COMPARISON, STRENGTHS AND LIMITATIONS

The current paper gives an overview of the different techniques and methods in the literature to extract wettability information from NMR data. Some techniques, for example field cycling, have virtually no applicability downhole due to the equipment required; others, such as the one based on T_2 , requires extremely good knowledge of the fluids and rock sample, which is knowledge that is only available in the laboratory. The most promising techniques with downhole applicability are, in our opinion, the one based

on saturation, the one based on T_1/T_2 ratio, and the one based on restricted diffusion. Each one of these techniques has strengths and limitations, and these are summarised in Table 1. Shales rocks have not been discussed in this paper, since the entire concept of wettability in shales is very debatable if not meaningless, with oil in oil wet pores and water in water wet pores.

Table 1: Strengths and limitations of the different techniques applicable downhole

	Saturation	T_1/T_2	Restricted Diffusion
Strengths	<ul style="list-style-type: none"> • Robust • Simple T_2 measurement 	<ul style="list-style-type: none"> • Simple and robust measurement • Possible for short T_2 (tight rocks) 	<ul style="list-style-type: none"> • Diffusion helps in fluid separation • Parameters need to be adjusted to see restriction
Limitations	<ul style="list-style-type: none"> • Requires DOI across invasion profile • Qualitative 	<ul style="list-style-type: none"> • Time consuming • Needs fluid separation 	<ul style="list-style-type: none"> • Impossible for short T_2

REFERENCES

- [1] A. Valori, F. Ali, W. Abdallah, Downhole Wettability: The Potential of NMR, SPE EOR Conf. Oil Gas West Asia. (2018). doi:10.2118/190332-MS.
- [2] W.G. Anderson, Wettability Literature Survey - Part 6: The effects of Wettability on Waterflooding, J. Pet. Technol. (1987).
- [3] W. Abdallah, J.S. Buckley, A. Carnegie, J. Edwards, B. Herold, E. Fordham, et al., Fundamentals of wettability, Oilf. Rev. 19 (2007) 44–61.
- [4] H.C. Torrey, Theory of Nuclear Spin Relaxation of Liquids for Large Surface-to-Volume Ratios, in: Bulletin Am. Phys. Soc., 1956: pp. 1–2.
- [5] R.J.S. Brown, Measurements of Nuclear Spin Relaxation of Fluids in Bulk and for Large Surface-to-Volume Ratios, Bulletin Am. Phys. Soc. (1956).
- [6] Korringa J., Interpretation of Data on Nuclear Spin Relaxation in Liquids for Large Surface-to-Volume Ratios, Bulletin Am. Phys. Soc. (1956).
- [7] R.J.S. Brown, I. Fatt, Measurements Of Fractional Wettability Of Oil Fields' Rocks By The Nuclear Magnetic Relaxation Method, in: SPE, Society of Petroleum Engineers, 1956. doi:10.2118/743-G.
- [8] A. Valori, G. Hursan, S.M. Ma, Laboratory and Downhole Wettability from NMR T_1/T_2 ratio, Petrophysics Vol. 58, No. 4 August 2017. 58 (2017).
- [9] W. Looyestijn, J. Hofman, Wettability Index Determination by Nuclear Magnetic Resonance, Proc. SPE Middle East Oil Gas Show Conf. (2005). doi:10.2118/93624-MS.
- [10] W. Looyestijn, J. Hofman, Wettability-Index Determination by Nuclear Magnetic Resonance, SPE Reserv. Eval. Eng. 9 (2006) 12–15. doi:10.2118/93624-PA.
- [11] W.J. Looyestijn, Wettability Index Determination from NMR Logs, in: SPWLA 48th Annu. Logging Symp., 2007: pp. 1–16.
- [12] A.S. Al-muthana, G.G. Hursan, S.M. Ma, A. Valori, B. Nicot, P.M. Singer, Wettability as a function of pore size by NMR, in: SCA2012 A013, 2012: pp. 1–12.
- [13] A.S. Al-muthana, G.G. Hursan, S.M. Ma, P.M. Singer, B. Nicot, A. Valori, et al.,

- US 2013/0261979 A1: Methods for determining wettability from NMR, US 2013/0261979 A1, 2013.
- [14] R. Freedman, N. Heaton, M. Flaum, G.J.J. Hirasaki, C. Flaum, M. Hurlimann, et al., Wettability, Saturation, and Viscosity Using the Magnetic Resonance Fluid Characterization Method and New Diffusion-Editing Pulse Sequences, *Proc. SPE Annu. Tech. Conf. Exhib.* (2002) 613–625. doi:10.2118/77397-MS.
- [15] J.J. Howard, Quantitative estimates of porous media wettability from proton NMR measurements, in: *Magn. Reson. Imaging*, 1998: pp. 529–533. doi:10.1016/S0730-725X(98)00060-5.
- [16] S. Al-Mahrooqi, An investigation of the effect of wettability on NMR characteristics of sandstone rock and fluid systems, *J. Pet. Sci. Eng.* 39 (2003) 389–398. doi:10.1016/S0920-4105(03)00077-9.
- [17] E. Johannesen, M. Steinsbø, Wettability characterization by NMR T₂ measurements in chalk, in: *SCA 2006*, 2006: pp. 1–8.
- [18] C.C. Minh, S. Crary, P.M. Singer, A. Valori, N. Bachman, G.G. Hursan, et al., Determination Of Wettability From Magnetic Resonance Relaxation And Diffusion Measurements On Fresh-State Cores, in: *SPWLA 56th Annu. Logging Symp.*, 2015.
- [19] M.D. Hurlimann, K.G. Helmer, L.L. Latour, C.H. Sotak, Restricted Diffusion in Sedimentary Rocks. Determination of Surface-Area-to-Volume Ratio and Surface Relaxivity, *J. Magn. Reson. Ser. A.* 111 (1994) 169–178. doi:https://doi.org/10.1006/jmra.1994.1243.
- [20] P.J. McDonald, J.P. Korb, J. Mitchell, L. Monteilhet, Surface relaxation and chemical exchange in hydrating cement pastes: A two-dimensional NMR relaxation study, *Phys. Rev. E.* 72 (2005). doi:10.1103/PhysRevE.72.011409|ISSN 1063-651X.
- [21] J. Mitchell, M.D. Hurlimann, E.J. Fordham, A rapid measurement of T₁ / T₂: The DECPMG sequence, *J. Magn. Reson.* 200 (2009) 198–206. doi:10.1016/j.jmr.2009.07.002.
- [22] K. Katika, M. Saidian, M. Prasad, I.L. Fabricius, Low-Field NMR Spectrometry of Chalk and Argillaceous Sandstones: Rock-Fluid Affinity Assessed from T₁/T₂ Ratio, (n.d.).
- [23] H. Guan, D. Brougham, K.S. Sorbie, K.J. Packer, Wettability effects in a sandstone reservoir and outcrop cores from NMR relaxation time distributions, *J. Pet. Sci. Eng.* 34 (2002) 35–54. doi:https://doi.org/10.1016/S0920-4105(02)00151-1.
- [24] B. Nicot, N. Vorapalawut, B. Rousseau, F. Luis, G. Hamon, J. Korb, Estimating Saturations in Organic Shales Using 2D NMR, *SCA. i* (2015) 1–12.
- [25] P.M. Singer, E. Rylander, T. Jiang, R. Mclin, R.E. Lewis, S.M. Sinclair, 1D and 2D NMR Core-Log Integration in Organic Shale, *SCA 2013.* (2013) 1–12.
- [26] J.-P. Korb, B. Nicot, A. Louis-Joseph, S. Bubici, G. Ferrante, Dynamics and Wettability of Oil and Water in Oil Shales, *J. Phys. Chem. C.* 118 (2014) 23212–23218. doi:10.1021/jp508659e.
- [27] J.P. Korb, M. WhaleyHodges, R.G. Bryant, Translational diffusion of liquids at

- surfaces of microporous materials: Theoretical analysis of field-cycling magnetic relaxation measurements, *Phys. Rev. E.* 56 (1997) 1934–1945.
- [28] S. Godefroy, J.P. Korb, M. Fleury, R.G. Bryant, Surface nuclear magnetic relaxation and dynamics of water and oil in macroporous media, *Phys. Rev. E.* 64 (2001) 1–13. doi:10.1103/PhysRevE.64.021605.
- [29] N. Bloembergen, E.M. Purcell, R. V Pound, Relaxation effects in nuclear magnetic resonance absorption, *Phys. Rev.* 73 (1948) 679–712.
- [30] V. Anand, Novel methodology for accurate resolution of fluid signatures from multi-dimensional NMR well-logging measurements, *J. Magn. Reson.* 276 (2017) 60–68. doi:<https://doi.org/10.1016/j.jmr.2017.01.007>.