

# **TORTUOSITY PREDICTION FROM OXYGEN DIFFUSION VIA $T_2(z, t)$ RELAXATION NMR**

Igor Shikhov and Christoph H. Arns  
University of New South Wales, Sydney, Australia

*This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Snowmass, Colorado, USA, 21-26 August 2016*

## **ABSTRACT**

Petrophysical interpretation of NMR responses may be affected by the presence of dissolved oxygen in the fluids saturating rocks. Oxygen shortens longitudinal and transverse relaxation times of liquids due to NMR paramagnetic relaxation enhancement (PRE). The presence of oxygen in solution and its effect on relaxation time of fluids is often considered unwanted requiring thorough purification and degassing of liquids for proper experimental conditions. However, the design of laboratory experiments to characterize saturated rock samples may require exposure of the bulk fluid or saturated solid sample to atmosphere while under field conditions air-saturated fluids may be introduced in the near well-bore formation. We utilize relaxation time contrast between air-saturated and oxygen-free fluids to evaluate transport properties of a porous system by observing the dynamics of oxygen concentration change and estimate the time required for equilibration. For the case of two phases, the diffusion of oxygen becomes dependent on local saturation, fluid distribution pattern and wettability since it may occur predominantly through connected continuous fluid patches. Using spatially-resolved  $T_2(z, t)$  experiments we derived time-dependent oxygen concentration change  $C_{O_2}(z, t)$  along a fully- and partially-saturated carbonate core plug exposed to air saturated oil at its inlet. This provided an effective mutual diffusion coefficient of oxygen and a tortuosity estimate. We compare with electrical tortuosity calculated on a micro-tomographic image of that core by solving the stationary Laplace equation for conductivity. We demonstrate that by solving a forward problem of finding an effective mutual-diffusion coefficient of oxygen it is possible to obtain a reasonable estimate of equilibration time and access tortuosity via NMR over longer length scales.

## **INTRODUCTION**

Formation waters and hydrocarbons at reservoir conditions are free from oxygen. Well operations may result in introduction of oxygen into near-wellbore parts of the formation through air-saturated drilling fluids. Even more likely is that air may be introduced in the cores in the laboratory during the SCAL experiments. Oxygen dissolved in fluids affects NMR relaxation and may lead to improper petrophysical interpretation. It may diffuse inside the rock following a particular connected fluid phase or diffuse between fluid

phases through their interface. Understanding these processes enables to correct the reduction of observed NMR relaxation time. Furthermore, use of oxygen as a tracer and access to NMR relaxation resolved in time and space provides a potential for enhanced petrophysical characterization of rocks subjected to contact with oxygen-saturated fluid. Transport and evolution of oxygen concentration have been routinely studied in medicine, chemical and bioengineering, soil sciences etc. These studies typically consider diffusion of oxygen in a single phase saturating the porous medium (soil or rock) [1]. The ability of alkanes to store and conduct oxygen much faster in emulsions than in pure aqueous solutions was studied [2] who reported a so-called “shuttle mechanism”. However, there is a gap in studies of oxygen as tracer in multi-phase transport through saturated porous systems in a petrophysical context. Paramagnetic species, including dissolved gaseous oxygen, are known to cause an enhanced relaxation to protons of a solvent, e.g. water or hydrocarbons. We describe the effect of paramagnetic enhancement (PRE) on observed relaxation time as a linear sum of oxygen-free bulk fluid relaxation rate and PRE related rate [3], [4]

$$\frac{1}{T_{1,2\,obs}} = \frac{1}{T_{1,2B\,pure}} + \frac{1}{T_{1,2\,O_2}}. \quad (1)$$

The latter term is a linear function of oxygen concentration [5], enabling direct estimation of oxygen concentration when end-point relaxation rates are known (fully oxygen saturated and oxygen free responses). We use a spatially resolved  $T_2(z,t)$  experiment to measure the change of relaxation time along the core length and to estimate oxygen concentration evolution. The latter is used to derive oxygen effective diffusion coefficient using an analytical solution to 1D concentration-diffusion equation.

## DIFFUSION OF A GAS TRACER IN A MULTI-PHASE SYSTEM

Oxygen present in liquids greatly increases relaxation rate of  $^1\text{H}$  of a host fluid due to interaction of magnetic moments of its protons and  $\text{O}_2$  outer unpaired electrons. Consider a rock partially saturated with oxygen-free water and oil having one boundary exposed to oil saturated with air and all other boundaries closed, (Fig.1). Air diffuses towards lower concentration along the core following two path-ways: (1) along the connected path of oil; (2) diffusion of gas across the interface is slow relative to diffusion within the continuous liquid face, yet still occurs at substantial rate. Air contained in oil will diffuse into the water and then spread along the water phase, which in water-wet rock is connected along the core length. This also offers a mechanism to connect isolated patches of oil. Diffusion of tracer dissolved gas with concentration gradient in liquid is described by Fick’s second law which leads to the unsteady state diffusion equation

$$C_t = D_e C_{zz}, \quad (2)$$

where  $C$  is concentration in the solution,  $t$  is time and  $D$  the mutual diffusion coefficient of tracer in the fluid. Boundary conditions are constant inlet concentration  $C(0,t) = C_0$  and

open at the outlet with side boundaries closed. For two fluids an additional boundary condition is set at the fluids interface proportional to the relative solubility gradient on both sides of the interface. We solved Eqn.2 using finite difference method on a regular mesh to calculate a change of oxygen concentration for a single fluid (Fig.1b, Fig.2a).

The solubility of oxygen in water in equilibrium with air is 8.5 mg/L at 25°C, while solubility in n-paraffins is almost an order of magnitude higher, 71 mg/L at 25°C for n-decane. Mutual diffusion coefficient of oxygen in n-alkanes is also much higher than that in water, although data is published only for n-hexane ( $9.9 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ) and n-hexadecane ( $2.46 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ). The expected value of oxygen diffusion in decane is in between, approximately  $6 \cdot 10^{-5} \text{ cm}^2/\text{s}$ . The analytical solution to Eqn.2 with relevant boundary and initial conditions is used to calibrate the numerical solution to physical dimensions

$$C(z,t) = C_0 (1 - \text{erf}\{z/\sqrt{(4Dt)}\}) , \text{ or} \quad (3)$$

$$\ln C = a - z^2 / (4Dt) \text{ for a semi-infinite medium ([6]).} \quad (4)$$

## **$T_2(z, t)$ SIMULATION AND EXPERIMENTAL PROCEDURES**

Mount Gambier limestone exhibits very high porosity,  $\phi_{\text{brine}}=52\%$  and permeability,  $k_{\text{brine}} = 4.47 \text{ D}$ . The majority of the pore space is associated with large pores (82% effective porosity is resolved at 10.95  $\mu\text{m}$  resolution). Fig.3a,b shows the effect of dissolved oxygen on NMR  $T_2$  relaxation for fully decane saturated core. Matching modes of MICP and  $T_2$  distributions in air-saturated and oxygen-free states requires application of a 60% lower effective relaxivity  $\rho_2$  for  $O_2$ -free oil case (10.5  $\mu\text{m/s}$  compared to 16.0  $\mu\text{m/s}$ ). The  $T_2(z,t)$  experiment utilizes CPMG at constant gradient 0.6 G/cm (frequency encoding) providing 3-mm spatial resolution.  $T_2(z)$  is averaged over a total acquisition time of two minutes.  $T_2(z)$  was obtained every 6, 8 or 18 minutes depending on samples.

The impact on mean relaxation time is very high when dealing with decane as a representation of light oil (Fig.3a). Interestingly, no difference between  $T_2$  distributions obtained on fully water saturated Mount Gambier core was observed irrespectively whether or not water was deoxygenated, while bulk water  $T_{2,B}$  shows an easily detectable difference (with  $T_{2B}$  of 3.2 and 2.5 sec respectively). This implies that such measurements are inherently sensitive to wettability conditions or certainly tells if rock is water-wet.

## **RESULTS AND DISCUSSION**

The contrast offered by oxygen to relaxation times of bulk fluids and saturated Mount Gambier rock is given in Table 1. No difference in  $T_{2LM}$  was observed in case of a fully water saturated sample. Decane can carry eight times more oxygen than water and offers four times greater contrast between oxygen-free and air-saturated fluid (in our experiments oxygen is always a fraction of that gas in the air, i.e. 0.209). Expectedly, partially saturated rock, where the water phase consists of deuterium oxide ( $D_2O$ ), shows

a larger difference between these states than fully decane saturated rock and less than bulk decane sample. This evidences partially oil wetting conditions.

Fig.4b,c demonstrates the time-evolution of oxygen concentration along the core (the first 6-7 3-mm thick slabs) calculated from  $T_2(z, t)$  experiments. Initially the core was fully saturated with deoxygenated n-decane, followed by exposure of the inlet to bulk decane equilibrated with air. Fitting to analytical solution results in the following oxygen effective diffusion coefficients: (1) bulk decane  $D_{e,O_2} = 6.9 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ; (2) Mt. Gambier at  $S_o=100\%$   $D_{e,O_2} = 6.1 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ; (3) Mt. Gambier at  $S_o=51\%$  (the rest is  $D_2O$ )  $D_{e,O_2} = 3.7 \cdot 10^{-5} \text{ cm}^2/\text{s}$ .  $D_e$ -based tortuosity,  $\tau_d$  is estimated as  $\tau_d = \varphi D_e / D_o$ . Another tortuosity value is obtained by solving Laplace equation for conductivity on a voxelized image,  $\tau_c = \varphi c_e / c_o$  assuming perfectly water-wet conditions (see Fig. 5). Tortuosity estimate based on oxygen diffusion is expectedly higher than conductivity since some transport is possible between two phases. It reasonably well captures change of tortuosity due to saturation decrease. Factors requiring further consideration include an exposure of a core to atmosphere prior to NMR experiment; deoxygenating fluids by substitution of air with pure nitrogen, and wettability conditions which may result in better oil connectivity.

## CONCLUSION

We demonstrated that the proposed approach can be applied for quantitative characterization of multi-fluid systems saturated rocks by exploiting relaxation contrast offered by oxygen solubility in aqueous and oil phases and their wettability. Interpretation of time- and spatially-resolved relaxation signal (typical in well-logging) may provide information about spatial fluid distribution. Furthermore, the approach can provide information which is difficult otherwise to obtain such as tortuosity, wettability, fluids interfacial area and potentially relative permeability. Alternatively, the approach may be used to correct NMR signal for oxygen related environmental effects.

## ACKNOWLEDGEMENTS

CHA acknowledges the Australian Research Council (ARC) for a Future Fellowship and the National Computing Infrastructure for generous allocation of computing time.

## REFERENCES

1. Aachib, M. *et al.*, 2004, *Water, Air and Soil Pollut.*, **156**, 163-193.
2. Bruining, W. J. *et al.*, 1986, *Chem. Eng. Sci.*, **41**, 1873-1877.
3. Chiarotti, G. *et al.*, 1955, *Il Nuovo Cimento*, **1**(5), 863-873.
4. Chen, S. *et al.*, 2004, *SPE ATCE, SPE90553, Houston, TX, USA*.
5. Parker, D. *et al.*, 1974, *Chem. Phys. Let.*, **25**(4), 505-506.
6. Crank, J., 1975, *The mathematics of diffusion*. Oxford: Clarendon Press.

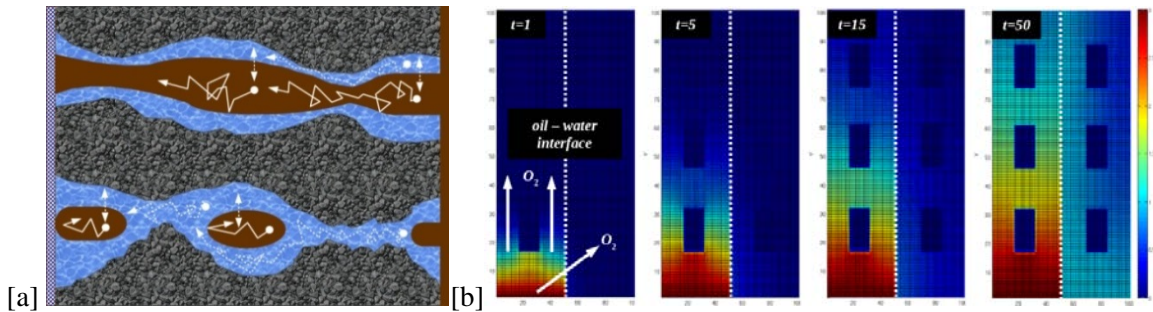


Fig.1: [a] Sketch of porous system saturated with wetting (water) and non-wetting (oil) fluids. Top: connected path of oil phase, bottom: isolated oil patches.  $O_2$  transport is expected to be much slower in the latter case. [b] Finite difference approximation to 2D concentration-diffusion equation illustrating change of concentration with time in presence of interface and different solubility of phases. Air dissolved in the oil diffuses from the high concentration at the inlet towards the low concentration primarily along the connected oil pathway.

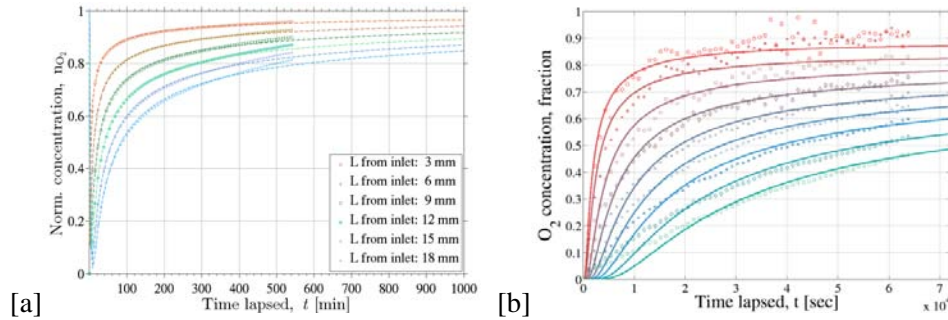


Fig.2: [a] Concentration of  $O_2$   $C(z,t)$  calculated using a finite-difference method (FDM) for 1D time-dependent concentration-diffusion equation  $C_t = D_e C_{zz}$  for six 3-mm slabs and [b]  $O_2$   $C(z,t)$  measured for bulk decane (a soaked sponge) using a  $T_2(z, t)$  experiment.

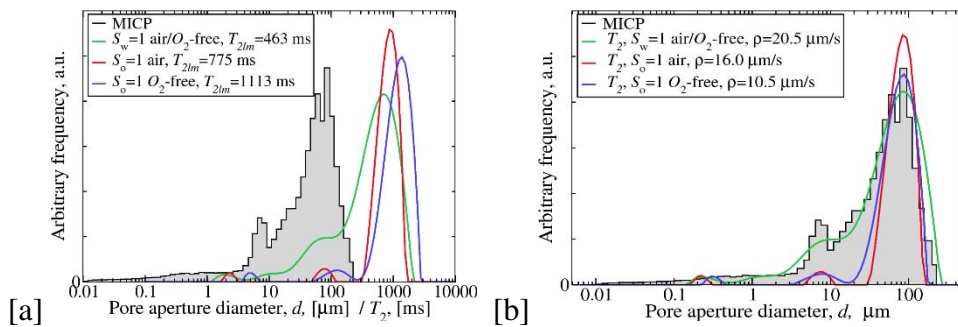


Fig.3: [a] Comparison of experimental  $T_2$  distributions of a core fully saturated with water or oil in equilibrium with air / oxygen free state. Shift is apparent in case of oil. [b] Shift of  $T_2$  responses to match mode MICP values at fully water and fully oil saturation states (air-saturated and  $O_2$  free).

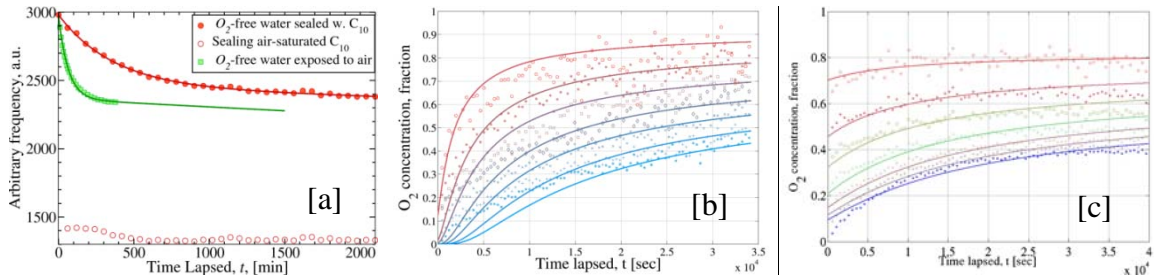


Fig.4: *Fluids only*: [a] Change of relaxation rate with time for deoxygenated bulk water sample exposed to air compared to air-saturated decane. The rate of oxygen concentration change is controlled by diffusion of air across the phases interface since the diffusion rate of oxygen in both cases is the same,  $2 \cdot 10^{-5} \text{ cm}^2/\text{s}$ . The change of average  $O_2$  concentration is 6~8 times higher in an air-water system comparing to decane-water one. *Mt Gambier*: [b,c] Change of oxygen concentration  $C(z, t)$  as normalized fraction of solubility with time at different distances from the core inlet evaluated from the  $T_2(z, t)$  experiment for the case of [b]  $So=100\%$  and [c]  $So=51\%$ . Distances  $L$  (to the middle of 3 mm slabs) are: 3, 6, 9, 12, 15 mm, etc.

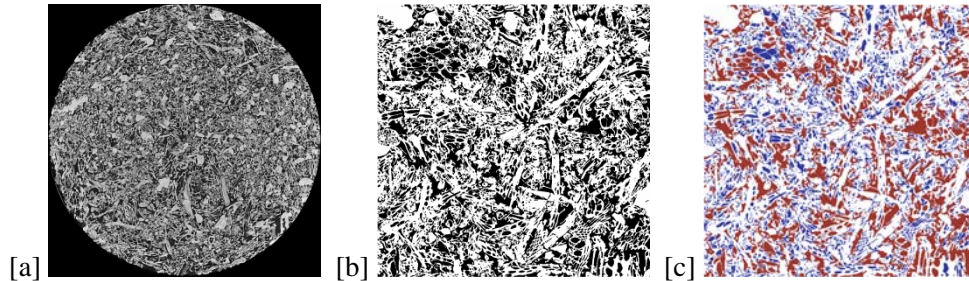


Fig.5: [a] Slice through the tomogram of Mt Gambier limestone at  $10.95 \mu\text{m}$  voxel resolution (2160x2160 voxel). [b] Subsection of two-phase solid-void segmented image (1440x1440 voxel). [c] Slice through capillary drainage transformation (CDT) to set fluid distributions assuming fully water-wet rock;  $So=48.9\%$ .

Table 1.  $T_{2LM}$  relaxation times of bulk fluids and saturated rock.

sample	air	O <sub>2</sub> -free	Ratio O <sub>2</sub> -free/air
bulk water	2470	3220	1.30
MtG, Sw=100%	463	463	1.00
bulk n-decane	1250	2850	2.28
MtG, So=100%	775	1113	1.44
MtG, So=51%+D <sub>2</sub> O	1077	1983	1.84

Table 2. Tortuosity estimated from  $\mu$ -CT image and  $T_{2LM}$  experiment.

sample	MtG, So=1.0	MtG, So=0.5	ratio
$T_2(z, t) - D_{e,O_2} : \tau_d$	0.451	0.248	1.82
Image, $c : \tau_c$	0.186	0.054	3.44