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T_2 –T_2 Exchange in Biofouled Porous Media

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Abstract

Recent two dimensional nuclear magnetic resonance (NMR) techniques access exchange in pore structures through surface relaxation and diffusion based relaxation [1-4]. This research applies these techniques to measure pore changes due to biofilm growth and the impact this growth has on diffusion transport. The porous media used in this study are model beadpacks constructed from borosilicate glass beads with diameters approximately 100 μm. This research shows that through changes in the relaxation rates, NMR can be used to verify biofilm growth in porous media.

Keywords

exchange, porous media, biofilm, borosilicate, magnetic resonance

1. Introduction

From water service utilities to food 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 such as supercritical CO_2 sequestration. To better understand the structure and transport changes that occur in biofouled porous media, this research applies recent two dimensional NMR techniques [1-4] to measure pore changes due to biofilm growth and the affect this growth has on diffusive transport. Previous studies by Mitchell *et. al* [4] use similar bead packs to quantify water exchange. The aim of this study is to use the richness of the T_2-T_2 distribution and in particular the presence, absence or change of the cross peaks as a function of the exchange time to detect the presence of biofilm and to determine its impact on the diffusive transport properties of the porous media.

2. Theory

T_2 relaxation in porous media is described differently depending on whether the spins are in the slow or fast exchange regimes. In slow exchange regimes, spins are either in the domain nearest to the pore walls where their relaxation is faster and dominated by surface affects like susceptibility and paramagnetic impurities, or they are in the bulk liquid regime in the pore center and their relaxation is close to pure water. A T_2 measurement in this regime will yield two populations of T_2 values. In the fast exchange regime, all spins experience the relaxing effects of the pore surface region and hence, measurements of the T_2 in the porous system will yield a single value that is dominated by the effects of the pore surfaces. [1]

The timescale of the transition between the slow and the fast exchange regimes depends on the time necessary for the spins to diffusively sample the entire pore region. Hence, the measured T_2 distribution for a particular timescale depends on the pore surface, the pore surface-to-volume ratio, and the viscosity of the imbibed fluid. T_2 -T_2 distributions have the ability to probe exchange between T_2 regions if the ratio of T_1/T_2 >1 and if the exchange time between the two encoding periods is appropriately chosen. The cross peaks in the distributions can yield information related to the spins diffusive transport between several different T_2 regions and these different T_2 regions may represent different size pores or different surfaces. The growth of biofilm in a porous media adds complications by adding an additional gel phase to the pores, changing pore connectivity, effective pore size, surface and bulk T_2, as well as introducing additional salts and paramagnetic impurities.

3. Experimental

The 100μm borosilicate glass bead packs were used to create a model bead pack. The 750mL BHI-salt solution media used to grow the biofilms is made of 13.5g brain heart infusion (BHI), 0.56g ammonium chloride, 30g sodium chloride, and 2.25g sodium nitrate. Using a sterile pump, the media was pumped at 0.3 mL per minute for three days to grow the *Bacillus mojavensis* biofilm.

The ARTDECO [5] sequence, shown in figure 1, and described by Washburn and Callaghan [3], shows both an initial and final CPMG [6] echo train separated by an exchange time, τ_m, during which transport can occur between T_2 domains. The sequence was repeated 128 times with a tau of 538 μs and mixing times ranging from 0.5-2 s in a 5.9 T magnetic field. The variable m increments each repetition logarithmically 128 times and ending with m=n. For our experiment n=1024. The resulting 2D data set was 128 x 1024. Two dimensional Laplace inversion [7] using Propsa (Magritek, Wellington, New Zealand) was used to obtain the T_2-T_2 maps through a 2D non-negative least squares algorithm. [8]

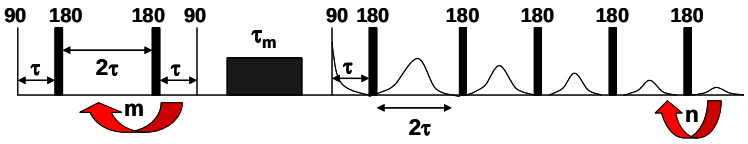

Fig. 1: The ARTDECO sequence was used to measure T_2 exchange. There are two CPMG [6] echo trains separated by an exchange time.

4. Results

For a variety of mixing times ranging from 0.5 s to 2.0 s, several T_2-T_2 maps were obtained for the borosilicate bead packs in three different liquid media: water, BHI-salt solution, and biofouled BHI-salt solution. A shift in the predominant diagonal peak from the water saturated (T_2=0.48 s) to the BHI-salt saturated borosilicate bead pack (T_2=0.30 s) is shown in figure 2. This reflects the decrease in bulk pore liquid T_2 due to the salts and biomolecules in the BHI-salt solution. After growing a biofim in the bead pack, there is a further shift of the main diagonal peak from 0.30 s to 0.12 s and visible cross peaks appear (figure 2). For

comparison, the T_1 values for the beads in water, BHI-salt solution, and biofouled BHI-salt solution are 2.74s, 2.24s, and 2.08s, respectively. This shows that biofilms do in fact grow inside porous media and that NMR can be used as a tool to determine impact on transport to surfaces and between pores. The T_2-T_2 maps are shown as log-log plots.

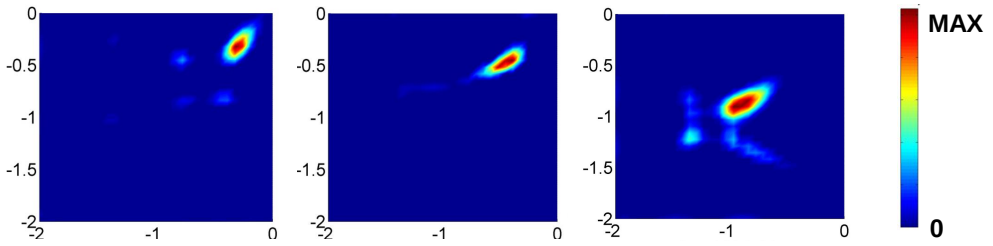

Fig. 2: Borosilicate glass beads saturated in water (left), in BHI-salt solution media (middle), and biofouled in BHI-salt solution media (right). All had a 1.0 s mixing time. The T_2 values for the main diagonal peaks shifted with the addition of media from 0.48 s to 0.30 s. After biofouling the bead pack in BHI-salt solution media T_2 values for the main diagonal peaks shifted further from 0.30 s to 0.12 s. Additionally, off diagonal peaks are visible which indicate exchange. The T_2-T_2 maps are shown on a log-log scale.

3. Conclusions

In the clean, monodispersed borosilicate beads, a strong T_2 peak is seen for bulk pore water with small cross-peaks suggesting evidence of a second peak which represents surface relaxation of spins near the bead surface where $T_1 \neq T_2$ [1,2]. The addition of growth media, BHI-salt solution, reduces the bulk pore T_2 value observed for the fluid. Biofilm growth in the beads causes a further reduction in the T_2 value of the main peak due to the restricted rotational mobility spin state of those within the biomass. The number of spins in the smaller T_2 population increases. This indicates a spin population shift towards the slow exchange regime due to the biofilm extracellular polymeric substance formation on the bead surfaces. Results indicate that by varying exchange times, T_2-T_2 measurements may be able to determine the extent of biofilm growth in an opaque porous media such as geological formations.

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