T_1-T_2* Relaxation Correlation – Speciation in Solid-Like Materials

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Introduction: Low field MR analyses most commonly rely on T_2 lifetime measurements. Modification of the T_2 measurement to include a T_1 dimension has made the T_1-T_2 measurement a very powerful analytical technique. The T_1-T_2 measurement is uniquely well suited to characterization of the pore size distribution in porous materials and speciation of ^{1}H bearing fluids in a wide variety of materials including foods [1-2]. However, in a wide range of materials the T_2 lifetime is too short to permit T_1-T_2 measurement.

In such cases a T_1-T_2^* measurement is a useful analog to the T_1-T_2 experiment. T_1-T_2^* measurement enables one to differentiate species as a function of T_2^* in one dimension and T_1 in the other dimension. The T_1-T_2* measurement permits speciation of ^{1}H in solid-like materials. Monitoring changes of the T_1-T_2^* coordinate, and associated signal intensity changes, reveals structural changes in samples monitored as a function of time.

Methodology: The measurement is a conventional bulk inversion recovery or saturation recovery measurement with full sampling of the resulting FID. The 2D distribution function $f(T_1, T_2^*)$ is recovered by inversion of the data set via a 2D Fredholm equation of the first kind, more commonly known as a 2D inverse Laplace transform.

The method is tested by monitoring change in the water environment and water population of initially dry but well cured 0.45 w/c mortars undergoing imbibition. The measurement may be spatially resolved through adiabatic inversion with slice selection as described by Vashaee [3] for a local T_1-T_2 measurement.

Results: The results of Fig. 1 show two water environments in a 0.45 w/c ratio mortar. The shorter lifetime T_1-T_2* population is assigned to interlayer water. The longer lifetime T_1-T_2* population is assigned to pore water. The minimum transverse lifetime observable is limited by the RF probe deadtime, which is significantly shorter than the minimum echo time in most instruments. The sampling time is dramatically less for T_1-T_2* being limited by the dwell time as opposed to the echo time for the T_1-T_2 measurement.

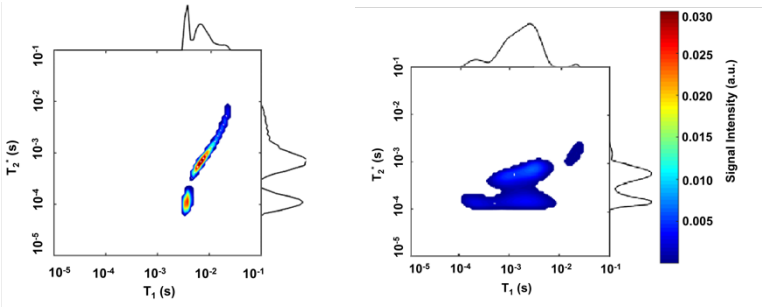

Fig. 1: Water population and environment change revealed by T_1-T_2* relaxation correlation measurement of an initially dry 0.45 w/c mortar imbibing water for 8 hours (left) and 132 hours (right).

The water populations and water environments change dramatically with imbibition of water as shown at 8 hours and 132 hours of imbibition. The permeability of such mortars is well known to change dramatically at times intermediate between these values [4]. As suggested by these results, there is a pore level change in morphology which reduces permeability.

Conclusion: The mortar imbibition example illustrates clearly the potential of this simple method to monitor change in population and environment of ^{1}H species in short signal lifetime systems inaccessible to T_1-T_2 measurement. The approach may however be generalized to many industrially significant solid-like systems where one seeks to determine composition.

References: [1] Song et al, JMR 2002. [2] Song, Prog NMR Spec 2009 [3] Vashaee et al, JMR 2018. [4] Taylor et al, J. Mat. Sci. Lett. 1999.