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NMR 1D-imaging of water infiltration into mesoporous matrices

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Abstract

It is shown that coupling nuclear magnetic resonance (NMR) 1D-imaging with the measure of NMR relaxation times and self-diffusion coefficients can be a very powerful approach to investigate fluid infiltration into porous media. Such an experimental design was used to study the very slow seeping of pure water into hydrophobic materials. We consider here three model samples of nuclear waste conditioning matrices which consist in a dispersion of $NaNO_3$ (highly soluble) and/or $BaSO_4$ (poorly soluble) salt grains embedded in a bitumen matrix. Beyond studying the moisture progression according to the sample depth, we analyze the water NMR relaxation times and self-diffusion coefficients along its 1D-concentration profile to obtain spatially resolved information on the solution properties and on the porous structure at different scales. It is also shown that, when the relaxation or self-diffusion properties are multimodal, the 1D-profile of each water population is recovered. Three main levels of information were disclosed along the depth-profiles. They concern (i) the water uptake kinetics, (ii) the salinity and the molecular dynamics of the infiltrated solutions and (iii) the microstructure of the water-filled porosities: open networks coexisting with closed pores. All these findings were fully validated and enriched by NMR cryoporometry experiments and by performing environmental scanning electronic microscopy observations. Surprisingly, results clearly show that insoluble salts enhance the water progression and thereby increase the capability of the material to uptake water.

Keywords: Porous media; Relaxation times; PFG-NMR; Restricted diffusion; Pore size; Bituminized waste product (BWP); Leaching

1. Introduction

The manifold measurements provided by nuclear magnetic resonance (NMR) are widely used to investigate fluid transport within porous media. This is indeed an area of continuing research in various disciplines, such as civil engineering, soil and food sciences. Studies on drying or infiltrating processes generally resort to imaging techniques in order to characterize the spatial evolution of the fluid concentration over time. To do so, a common method consists in studying the fluid transport and/or the associated matrix swelling or shrinking in the axial symmetry of cylindrical samples by NMR 1D-imaging. Examples in the literature include, for instance, works on polymer membranes [1], organic hydrogels [2, 3], catalytic materials [4, 5] or porous building media [6]. Other studies resort to relaxation and self-diffusion experiments in order to understand how the fluid locally progresses and how the micro- and nanostructure of the material evolve. For instance, such approaches have been recently applied to investigate the modifications of the internal structure of gypsum [7, 8], cement pastes [9], and pharmaceutical pellets [10] caused by water absorption. Nevertheless, in contrast to imaging experiments, relaxation and self-diffusion measurements are averaged on the sample volume. Therefore, results generally consist in distributions of values that cannot be directly related to the macroscopic variations of the sample structure and composition induced by the fluid progression.

Studies that resort to NMR experiments with 1D spatial encoding are not so common even though they provide data that are spatially resolved along the sample depth-profile, thereby making possible to relate the information provided by the relaxation and self-diffusion measurements to the local sample composition. Such methods have nevertheless

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proven their efficiency for characterizing the spatial dependence of micrometric droplet sizes in emulsified samples [11–13]. In this paper, we attempt to illustrate that combining NMR 1D-imaging with relaxation and self-diffusion studies can be a powerful method to investigate infiltrating or drying processes. To do so, we resort to an interesting approach that couples a specific NMR sequence, as spin-system preparation, with 1D-imaging, as signal acquisition mode [11], and use it to investigate the moisture progression in some hydrophobic materials that are submitted to a unidirectional water infiltration. Beyond the water concentration 1D-profile at the macroscopic scale, the spatial dependence of the nano- and microporous structures is thus investigated along the depth-profiles by means of the relaxation or self-diffusion measurements, respectively.

The materials studied are called bituminized waste products (BWP) and consist in a dispersion of different salt grains, which contain a very small fraction of radioactive elements, embedded in a bitumen matrix [14]. Indeed, in France, a part of the low and intermediate radioactive elements coming from the effluents of the nuclear industry has been managed by their incorporation in bitumen. It is now established that the interaction of BWP with water in storage zones can lead to some material modifications, and hence deteriorate the conditioning over a very long period of time. Previous studies on the leaching of BWP have allowed scientists to put forward constitutive models aiming at predicting the kinetics of water uptake and salt release as well as the matrix microstructure deformation in the leached layer [14–16]. In this context, our study was motivated by the need of better characterizing the behavior of BWP when brought in contact with water before refining the current models. More precisely, our goal was threefold: (i) to determine whether the wetting front is limited by the dissolution front of the soluble salts ($NaNO_3$), (ii) to check for a possible influence of the insoluble salts ($BaSO_4$) on the water uptake kinetics, and (iii) to study the water dynamics as well as the sample structure over a wide range of length scales in the leached zone.

Three inactive and model BWP samples varying by their composition in embedded salts are studied. After a chemical and structural characterization of the unleached materials (Section 4.1), a first set of NMR and 1D-imaging experiments is used to investigate the kinetics of water uptake and the moisture progression as a function of sample depth (Sections 4.2 and 4.3). 1D-imaging measurements of relaxation times and self-diffusion coefficients are then exploited to locally characterize the altered matrices along their depth (Sections 4.4 and 4.6). Results provide information on the salinity of the infiltrated solution and on the structure of the porosity at different scales: an open network coexisting with closed pores at the micrometer scale, hindrance of the molecular dynamics in the wetting front, etc. All our findings are discussed in relation to the composition of the different samples. They are confronted to an NMR 1D-imaging melting temperature study (Section 4.5) and to environmental scanning electronic microscopy (ESEM) observations of the leached samples (Section 4.7).

2. Materials

Three synthetic bituminized materials varying by their embedded salts were studied. Sample preparation procedures (Fig. 1) were optimized to recover a final mass percentage of salts of about 40% in all materials. They all have been produced with the same bitumen composition (Azalt 70/100) and with the same operating conditions. Pure bitumen was inserted at a temperature of 140°C at the beginning of a co-rotating twin screw extruder (Werner ZSK25WLE: L=1000 mm, L/D=40, C_l=21.1 mm with L the length, D the screw diameter and C_l the centerline distance) operating at a screw speed of 70 rpm with a flow rate of 0.57 kg h^{-1}. Sludge, which contained water with dissolved $NaNO_3$ and/or insoluble $BaSO_4$ grains, was inserted 5 cm further at room temperature. Toluene and surfactants were added at the same inlet to make the sludge–bitumen mixture more fluid. Four vapor outlets were used along the screw to enable water evaporation (remaining quantity <1% in the final products). Consequently, crystallization of soluble salts occurred during the extrusion process. All the produced materials were thus composed of salt grains embedded in bitumen. Table 1 gathers the main parameters related to the chemical composition of the different samples. For the sake of clarity, S-type stands for samples that only contain soluble salts, I-type stands for samples that only contain insoluble salts and B-type stands for samples that contain both soluble and insoluble salts.

3. Methods

3.1. Leaching experiments

Leaching experiments were performed in 10-mm-diameter NMR tubes in order to follow the progression of the wetting front as a function of time by 1D-imaging techniques. To prepare a sample, a handmade cylinder of

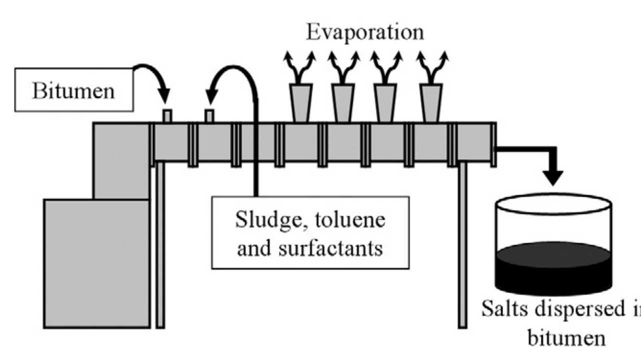

Fig. 1. Schematic representation of the extrusion process used to prepare the samples. Final materials consist in soluble and/or insoluble salt grains dispersed in bitumen.