
● Short Communication

**NMR IMAGING APPLICATION TO THE STUDY OF
ADSORPTION/PRECIPITATION OF CHEMICALS INSIDE POROUS MEDIA**

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Chemical inhibitors are widely used to prevent undesired precipitation of salts (e.g., CaCO_3 or CaSO_4) inside formations. The phase behaviour of solutions of phosphine-polyacrylic acids, (PPAA) which belong to a widely used class of threshold inhibitor, investigated in presence of Ca^{2+} ions and placed in a column packed with quartz sand. Solutions were prepared using deuterated water (99.9%) as solvent. T_1 -weighted spin-echo images gave profiles of the distribution of phosphine-polyacrylic acids during flow of the solutions inside the sandpack, while spatially resolved T_2 estimation (by nonlinear least-square fitting of several images acquired by varying the echo time) allowed precipitation phenomenon to be probed. In fact, spin-spin relaxation, which is particularly sensitive to slow motions, was affected by a precipitation process that caused a relevant T_2 decrease in the area of interest. No adsorption occurred under the conditions adopted, whereas precipitation was visualized at the interface area between the different solutions. The phenomenon was very slow and was mainly governed by diffusion of the chemicals. © 1998 Elsevier Science Inc.

Keywords: Magnetic resonance imaging; Flow; Precipitation in porous media.

INTRODUCTION

Precipitation inhibitors are generally injected into hydrocarbon formations to prevent crystal nucleation of undesirable salts, i.e., CaCO_3 or CaSO_4 , which would cause serious problems of scale formation during oil production.¹ Phosphine-polyacrylic acids (PPAA) belong to a widely used class of threshold inhibitors. This kind of technical application is mainly based on a complex mechanism of adsorption/precipitation within the well that allows a slow release (solubilisation) of the inhibitor molecules in the fluids during oil production. However, there is a poor knowledge of the phase behaviour of chemicals inside the porous medium. Experimental data for this kind of process are generally obtained by indirect methods such as chemical analysis of the effluents, without any information on local inhibitor placement and interaction with the surface. Nuclear magnetic resonance (NMR) methods could constitute a direct and noninvasive tool to study this kind of phenomena occurring inside the porous media of interest. In this work, NMR imaging techniques were applied to discriminate between adsorption and/or precipitation processes.

MATERIALS AND METHODS

The magnetic resonance imaging study, performed at 85 MHz ^1H NMR resonance frequency on a SISCO (Varian, Palo Alto, CA, USA) instrument equipped with a 2-T, 31-cm bore magnet, was applied to investigate the behaviour of PPAA (0.5%, w/w, in brine). PPAA is a commercial product (Servo, Delden, Holland) while brine was synthetically prepared using deuterated water (99.9% from Aldrich Chemical Co., Rouses Point, IL, USA) and NaCl (25 g/L). All the chemicals and the quartz sand (Aldrich for chromatography) used to pack the perspex column (1 in. in diameter $\times$ 5.5 in. in length), were carefully dried under vacuum in an oven. The packed column was placed inside a solenoidal coil for dynamic measurements. The flow experiments were realised at constant rate (30 cm^3/h) using Teflon tubing connected to a Hitachi pump (Hitachi, Tokyo, Japan) used for liquid chromatography.

RESULTS AND DISCUSSION

After conditioning of the packed column with synthetic brine (no appreciable NMR signal was given), 2

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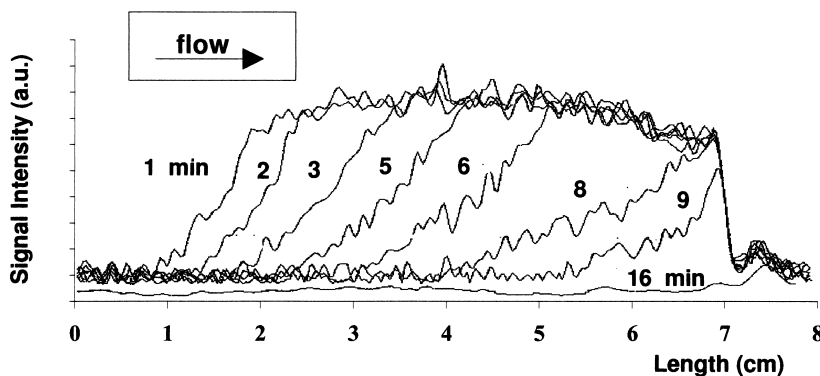


Fig. 1. Signal-intensity profiles (arbitrary values) showing distribution of PPAA along the column during D_2O injection (from left to right). Signal profiles were acquired by one-dimensional null-point imaging ($TE = 4$ ms, $TR = 0.5$ s, $T_{inv} = 0.2$ s, slice thickness 5 mm, 16 averages).

pore volumes (PV) of a solution of PPAA are injected and shut in for one night. Then, the solution of PPAA was displaced with brine, and PPAA profiles were obtained by one-dimensional imaging (Fig. 1). T_1 -weighted slice images of the profiles of the inhibitor along the column were acquired with a null-point spin-echo imaging sequence² (echo time (TE) = 4 ms, repetition time (TR) = 0.5 s, 16 averages). The inversion time ($T_{inv} = 0.2$ s) and repetition time were carefully calibrated to

suppress residual water signal (HDO molecules) mainly derived from mobile protons present in carboxylic groups of the PPAA by quick exchange with D_2O . Replacing water with D_2O clearly affects relaxation times of protons because of isotopic dilution, making the NMR method very sensitive to spin dynamics.³ After 16 min (2 PV injected), the PPAA was completely displaced (Fig. 1), indicating a negligible interaction between inhibitor molecules and the quartz sand at the interface (no appreciable adsorption). After saturation with a solution of $CaCl_2$ (2%, w/w, Ca^{+2}), PPAA was flushed (0.5 PV), and the injection was followed (Fig. 2a) to evaluate eventual precipitation phenomena. When the flushing was stopped, about half the column was occupied by the inhibitor, whereas the other half was saturated by incompatible $CaCl_2$ solution. After 1 h, the signal began to decrease at the interface (Fig. 2b). Spatially resolved T_2 profiles (obtained by pixel interpolation of several images, acquired by varying the echo time and fitted to

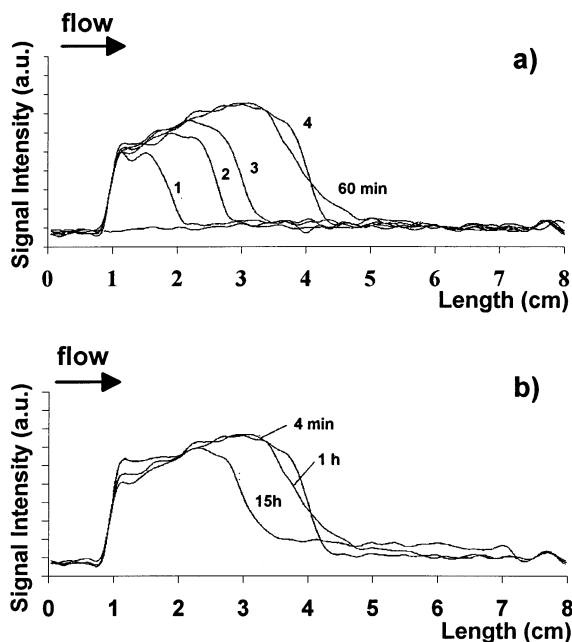
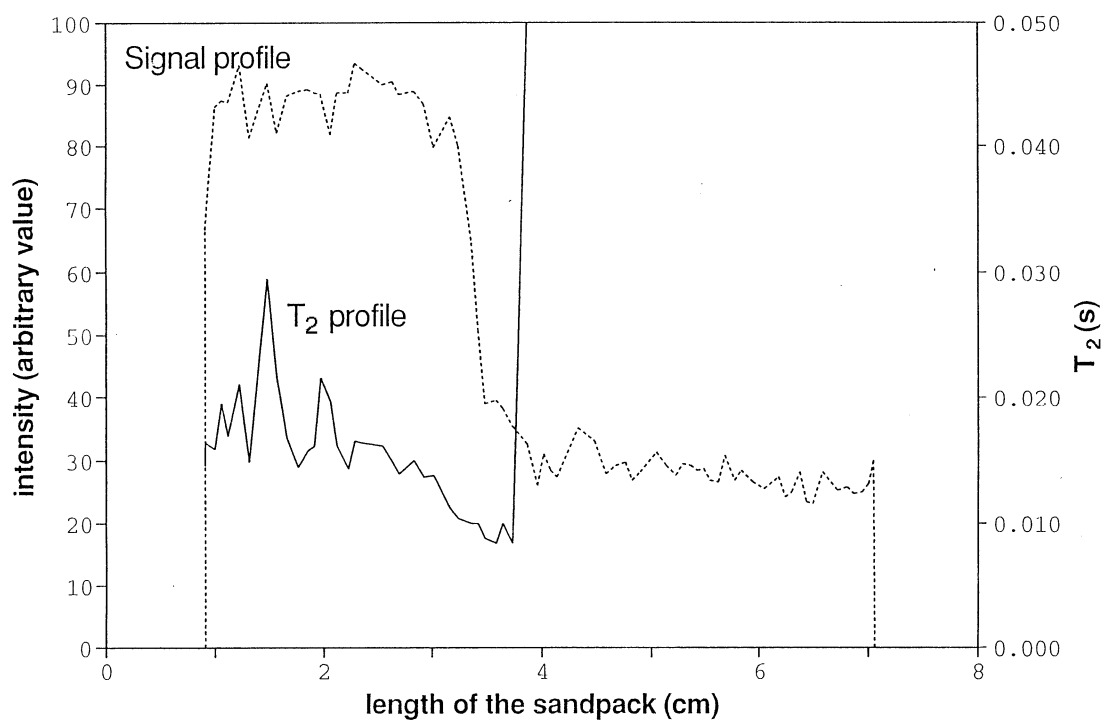


Fig. 2. Signal-intensity profiles (arbitrary values) showing distribution of PPAA along the column during injection (a) and after shut-in (b) in the sandpack saturated with Ca^{2+} (2%, w/w). Signal profiles were acquired as described in Fig. 1.

Fig. 3. (Top) Signal-intensity profiles (arbitrary values) showing distribution of PPAA along the column at the shut-in step are plotted with a one-dimensional T_2 profile (second axis on the right). T_2 profile was obtained by fitting to a single exponential decay curve the pixels intensity of several images acquired by varying the echo time.

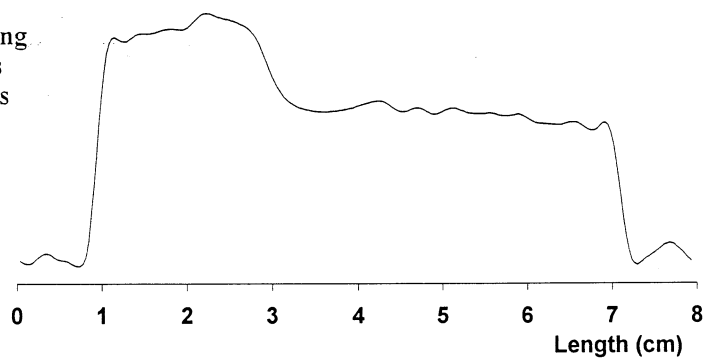
Fig. 4. (Bottom) Signal-intensity profiles (arbitrary values) showing distribution of PPAA along the column at the shut-in step obtained by varying the parameters in the acquisition sequence. (a) spin-echo sequence ($TR = 10$ s, $TE = 4$ ms); (b) inversion-recovery sequence giving T_1 filtering ($TR = 0.5$ s, $TE = 4$ ms, $T_{inv} = 0.2$ s); (c) spin-echo sequence with T_2 filtering ($TR = 10$ s, $TE = 32$ ms).



a) no filtering

TR = 10s

TE = 4ms

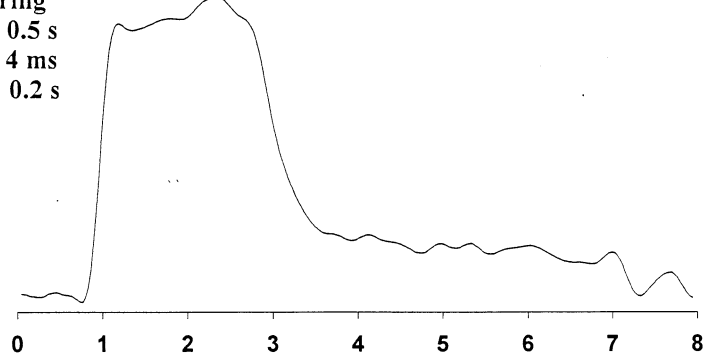


b) T_1 filtering

TR = 0.5 s

TE = 4 ms

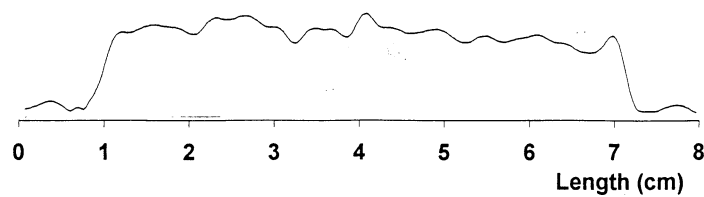
T_{inv} = 0.2 s



c) T_2 filtering

TR = 10s

TE = 32 ms



a single exponential decay curve)⁴ allowed precipitation phenomenon to be probed. In fact, spin-spin relaxation, which is particularly sensitive to slow motions, was affected by the precipitation process, which caused an appreciable T_2 decrease in the area interested (Fig. 3). The increase of signal in the rest of the column is due to HDO migration, which diffuses faster than polymer and was less efficiently suppressed when conditions changed, probably because of mixing of fluids. This was controlled by varying sequence parameters and creating mobility discrimination of the different molecules⁵ (Fig. 4); T_1 filtering minimised HDO (high T_1 and T_2 compared to polymer molecules) as shown in Fig. 4b, while T_2 filtering ($TE = 32$ ms) recovered mainly the HDO signal due to much shorter T_2 of PPAA low mobile molecules (Fig. 4c).

CONCLUSIONS

Magnetic resonance imaging methods have good potential for investigating chemical and physical processes related to interaction of chemicals inside porous media. No appreciable adsorption of the inhibitor (PPAA) on the quartz sand occurred under the conditions adopted, whereas precipitation was visualised at the interface area between the different solutions. The phenomenon oc-

curred very slowly and was mainly governed by diffusion of the chemicals, and precipitation of PPAA was not extensive.

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REFERENCES

1. Oddo, J.E.; Tomson, M.B. The solubility and stoichiometry of Calcium-DTPMP in brine solutions. *Appl. Geochem.* 5:527–532; 1990.
2. Fisher, A.E.; Balcom, B.J.; Fordham, E.J.; Carpenter, T.A.; Hall, L.D. A fast inversion recovery NMR imaging technique for mapping two-dimensional tracer diffusion and dispersion in heterogeneous media. *J. Phys. D: Appl. Phys.* 28:384–397; 1995.
3. Williams, J.L.A.; Maddinelli, G.; Taylor, D.G. Selective magnetic resonance imaging of chemicals in sandstone cores during flow. *J. Magn. Reson.* A109:124–128; 1994.
4. Antti, J.L.; Nieminen, O.K.; Koenig, J.L. Calculation of T_1 , T_2 proton spin density images in NMR imaging. *J. Magn. Reson.* 85:95–110; 1989.
5. Blumler, P.; Blumich, B. Magnetization filters: Applications to NMR imaging of elastomers. *Magn. Reson. Imaging* 10:779–788; 1992.