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# Visualization of colloid transport through heterogeneous porous media using magnetic resonance imaging

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## Abstract

The effects of heterogeneous grain packing on colloid transport were evaluated in flow-through columns using magnetic resonance imaging (MRI). Two columns were packed, each with a core of fine-grained silica gel surrounded by a shell of coarse-grained silica gel. In column 1, 600–850 μm silica gel was surrounded by 850–1000 μm silica gel. In column 2, 250–600 μm silica gel was surrounded by 850–1000 μm silica gel. Both columns were continuously purged with water and colloids were introduced as pulses.

MRI images of column 1 showed that colloid transport in the core and shell was not distinguishable. However, colloid transport was slightly faster along the bottom of the column. $T_1$-weighted images showed that small variations in the packing density of silica gel caused this effect. MRI images of column 2 showed that colloid transport in the core was much slower than colloid transport in the shell. Colloid exchange between the shell and the core was also observed.

Colloid transport velocities and collision efficiencies were calculated from the images. In agreement with the visualization, velocities for column 1 increased from the top to bottom of the column and velocities for column 2 were greater in the shell than in the core. Collision efficiencies were calculated, but trends were not apparent because of the difficulty of applying filtration theory to heterogeneous media. Velocities from images were compared to those from conventional experiments where colloid concentrations were measured at the column effluent. While often comparable, results from the latter mask many of the complexities that control the overall rate of colloid transport. Since these complexities can give rise to very different transport behavior, it is critical to understand their effects in real systems. Hence, MRI is a technique that has the power to elucidate many of the small-scale processes that affect the behavior of colloids in the field.

*Keywords:* Colloid transport; Magnetic resonance imaging; Attachment

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## 1. Introduction

Colloids are ubiquitous in many groundwater aquifers. They originate from weathering processes of the aquifer matrix, degradation of biological material and from precipitation of supersaturated solutions [1]. Under certain conditions, colloids may facilitate the transport of hazardous substances, such as radionuclides [2,3], heavy metals [4,5] and organic substances [6,7]. It is therefore of great interest to predict colloid transport.

Colloid transport is very sensitive to hydrochemical and hydrodynamic conditions. Conventional methods to investigate colloid transport often involve column studies, where colloid concentrations are measured at the column effluent or at selected points along the column length. Unfortunately, such methods do not clearly distinguish how spatial and temporal changes in hydrochemical and hydrodynamic conditions affect colloid transport. For example, breakthrough curves (BTCs) obtained from column effluent represent some average behavior of colloids in the column. Since different heterogeneous realizations can contribute to such BTCs, the processes that control colloid transport in the column are obscured.

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Conventional methods also have the potential to disrupt in situ conditions [8,9]. For example, large volume or quickly withdrawn samples can disrupt the local flow field or alter column chemistry, thereby yielding results that do not represent those in undisturbed columns. Consequently, non-invasive in situ and fast detection techniques are required to resolve colloid transport.

Promising non-invasive detection techniques include γ-ray tomography, positron emission tomography (PET), X-ray tomography and synchrotron radiation. γ-Ray and PET are sensitive to radioactivity. Colloids tagged with radioisotopes can be imaged at resolutions approaching 5 mm × 5 mm × 5 mm [10]. The acquisition time is on the order of 30 min/picture. X-ray tomography is sensitive to changes of density in a system. The acquisition times for X-ray tomography are in the range of minutes per image. For colloids that are denser than water, static images can be obtained at resolutions approaching 40 μm. With syncrotron radiation, colloids in aqueous solution can be characterized in situ with a spatial resolution below 100 nm. Chemical properties of the colloids can also be measured [11,12]. The typical thickness of a synchrotron sample for colloid detection should not exceed some micrometres, which makes this technique unsuitable for column studies. The acquisition time for synchrotron images is slightly longer than that for X-ray tomography.

Another promising non-invasive detection technique is magnetic resonance imaging (MRI). MRI is sensitive to changes in the local magnetic field. The local magnetic field can be altered in a controlled way by selective excitation of magnetically susceptible nuclei. MRI is robust in that it can be applied to many different systems. For example, MRI has been used to visualize the pore is space [13,14], to image non-aqueous phase liquids in porous media [15,16] and to measure the flow velocity and the self diffusion coefficient of water with [17,18] and without [19,20] the use of paramagnetic tracers. MRI is also robust in that high resolution images can be obtained in short time periods. Typical imaging times with spin-echo sequences are in the range of less than one minute. By using echo-planar imaging sequences, the time for one single image can be reduced to fractions of a second [21]. However, the latter technique is more sensitive to susceptibility artifacts which are common in natural porous media.

In this study, the transport of colloids through two heterogeneous columns packed with different size fractions of silica gel is quantified using MRI. Each column contained a coarse-grained shell of silica gel (850–1000 μm) surrounding a finer-grained core (either 600–850 or 250–600 μm). Superparamagnetic colloids were introduced to each column as a pulse and images were taken at selected time intervals during breakthrough. Colloid advection and dispersion rates and collision efficiencies calculated from MRI results are compared between columns, and to those determined from conventional tracer and colloid breakthrough curves. The objectives of this study are to illustrate how MRI can be used to resolve colloid transport mechanisms in situ and to understand how transport at the column scale is affected by transport at finer scales.

## 2. Experimental

### 2.1. Materials

Experiments were performed with a glass chromatography column, (i.d. = 1 cm, length of filter (L) ≈ 75 mm) equipped with Teflon fittings and frits (pore diameter 25 μm) at each end (Omnifit, Cambridge, UK). Three different sizes of silica gel (Selecto Scientific, Suwanee, GA) were used, 250–600, 600–850 and 850–1000 μm. All silica gel was washed, sieved and soaked in distilled deionized water (DDI water) for at least 48 h. After soaking, silica gel was packed into one of two columns under water. Column 1 had a 6 mm core of silica gel with a diameter of 600–850 μm, surrounded by a shell of silica gel with a diameter of 850–1000 μm. Column 2 had a 6 mm core of silica gel with a diameter of 250–600 μm, surrounded by a shell of silica gel with a diameter of 850–1000 μm. The tubing to and from the column was Teflon.

Pulse input experiments under saturated flow conditions were performed with nitrate as a conservative tracer ($NaNO_3$, Sigma–Aldrich), fluorescent polystyrene colloids (Duke Scientific, Palo Alto, CA) and superparamagnetic polystyrene-coated colloids (ME03N, Bangslabs, Fishers, IN). Columns were continuously purged with DDI water at 9 mL/h using a syringe pump (Cole Palmer 74900 series, Vernon Hills, IL). Pulses of water with the tracer or colloids were delivered from the bypass loop (0.11 mL) of a six-port valve (Upchurch Scientific, Oak Harbor, WA).

The input pulse concentration for the tracer was 20 mg/L $NO_3$. In previous experiments [22], $NO_3$ showed negligible retardation and thus is considered a conservative tracer. The concentration of $NO_3$ at the column effluent was measured on-line with a UV–vis spectrometer (Shimadzu UV 2401-PC, Columbia, MD) at 220 nm using a 300 μL flow-through cell. There was no evidence of degradation of $NO_3$ on the timescale of the experiment, i.e., the recovery was 1.0.

Both 1.01 and 1.96 μm fluorescent colloids were used. They were surfactant free and the reported particle density was 1.05 g/cm$^3$. The input pulse concentrations for the 1.01 and 1.96 μm colloids were $3.6 \times 10^{11}$ and $4.8 \times 10^{10}\,L^{-1}$, respectively. The concentration of the colloids at the column effluent was measured on-line with an Aminco/Bowman Series 2 spectrofluorimeter (Thermo Spectronic, Rochester, NY) at $\lambda_{ex} = 520$ nm and $\lambda_{em} = 575$ nm using a 300 μL flow-through cell.

The superparamagnetic colloids were 1.28 μm in diameter and they were coated with COOH-functional groups. The reported particle density was 1.726 g/cm$^3$. The particles were super paramagnetic, possessing negligible magnetic remanence and hysteresis. Pulse input concentrations of $1.3 \times 10^{12}$ and $1.1 \times 10^{12}\,L^{-1}$ were used in columns 1