

Mobility of Superparamagnetic Nanoparticles in Porous Media

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ABSTRACT

As the global demand for energy continues to soar, novel nanotechnologies (e.g., nanosensor) hold promise to improve oil reservoir characterization and enhance oil production. An understanding of the physical and chemical processes that govern nanoparticle transport and retention in reservoir matrices is critical for the implementation of such techniques. In this study, column experiments were conducted to measure the transport of superparamagnetic iron oxide nanoparticles (nMag) in a quartz sand saturated with a representative brine solution (2% *wt* CaCl₂ + 8% *wt* NaCl). nMag transport behavior was evaluated as a function of particle mass loading, sulfonate fraction in the polymer coating, and the presence of surfactants. Experimental results indicate that greater nMag mobility and lower retention were observed as the applied concentration (1,000 vs. 30 mg/L) and pulse width (3.2 vs. 0.16 pore volumes) were increased, indicating that the porous medium exhibited a maximum or limited capacity to retain nMag nanoparticles. A decrease in the ratio of 2-acrylamido-3-methylpropanesulfonate (AMPS) to acrylic acid (AA) in coating copolymers from 3:1 to 1:1, increased the retention of nMag by a factor of 2. At the lower input concentration (30 mg/L), more than 68% of total input nMag mass migrated through the column in the presence of 1,000 mg/L STEOL[®] CS-330, an anionic surfactant, while complete retention was observed in the presence of 1,000 mg/L Tween[®] 80, a non-ionic surfactant. These experimental results demonstrate the dependence of nMag mobility on both reservoir and nanoparticle surface properties under high salinity conditions.

Keywords: nanoparticles, mobility, porous media, reservoir, EOR

1 INTRODUCTION

The global demand for energy continues to increase, with a projected value of 1×10^{21} J by 2050 [1]. Since traditional fossil fuels (e.g., oil and gas) are likely to dominate the world energy supply for some time, improvements in reservoir characterization and oil production will be necessary to meet future energy needs. Nanoscale-based sensor technologies hold considerable promise as downhole reporters, however, their delivery, and subsequent recovery, in reservoir formations is one of the key challenges faced by these technologies. Consequently,

improved knowledge of the processes governing nanoparticle transport and retention in porous media under reservoir conditions is critical to the success of these approaches. The objective of this study was to systematically assess the mobility of nanoparticles in porous media as a function of particle mass loading, sulfonate fraction in polymer coating, and the presence of surfactant. The transport of superparamagnetic iron oxide nanoparticles (nMag) coated with grafted sulfonated copolymers in quartz sand was measured in a series of column experiments under brine conditions.

2 EXPERIMENTAL METHODS

2.1 Nanoparticle Preparation

Stable nMag particles grafted with poly(2-acrylamido-3-methylpropanesulfonate-*co*-acrylic acid) (PAMPS-PAA) were prepared following an established protocol that included processes of synthesizing copolymer, coating nanoparticle surface, and grafting the coated polymers [2-4]. The PAMPS-PAA copolymers were synthesized by addition of acrylic acid (AA) to a flask that was charged with 2-acrylamido-3-methylpropanesulfonate (AMPS) monomer, potassium persulfate and sodium metabisulfite under an atmosphere of nitrogen and with stirring. The reaction temperature was maintained at 80 °C in an oil bath for 16 h. The reaction mixture was then cooled to room temperature (23 ± 1 °C) and water was removed under reduced pressure until a constant mass was reached. The molar ratios of AMPS to AA used in this study were 3:1 and 1:1. To prepare nanosized iron oxide nanoparticles, ferrous and ferric chlorides (1:2 molar ratio) were dissolved in 40 mL of deionized water (DI) under a nitrogen gas atmosphere. When the temperature reached 90 °C, an aliquot (8 mL) of NH₄OH solution (30% *wt*) was injected into the reaction mixture to nucleate the iron oxide nanoparticles. After cooling, purification and introduction of amine groups, PAMPS-PAA was grafted onto the particles by formation of amide bonds [5]. The excess copolymers that were not grafted to the nanoparticle surfaces were removed by centrifugation. The particles were then redispersed by probe sonication. The prepared nMag-PAMPS-PAA stock was stored at room temperature.

2.2 Column Experiments

The 40-50 mesh ($d_{50} = 355 \mu\text{m}$) fraction of F-50 Ottawa sand (U.S. Silica, Berkeley Springs, WV, USA) was used as the porous medium for all column studies. Prior to use, the sand was thoroughly cleaned using a sequential acid wash, water rinse, ultrasonication, and oven-drying procedure [6]. For each transport experiment, a borosilicate glass column (2.5 I.D. \times 10 cm L.; Kontes, Vineland, NJ, USA) was packed with dry sand in 1-cm increment. To support packed sand and promote uniform flow of the aqueous phase, each column endplate was fitted with a 60-mesh stainless steel screen and a 70- μm nylon membrane. The packed column was then purged with CO_2 gas for at least 15 min to facilitate dissolution of air that was entrapped during the process of water imbibition. At least 10 pore volumes (PVs) of degassed brine solution (2% wt CaCl_2 + 8% wt NaCl) adjusted to pH 7 using 0.1 M NaOH were introduced to the column using a high-performance liquid chromatography (HPLC) pump in an upflow mode. Following complete saturation of the medium with brine solution, a pulse of nMag-PAMPS-PAA suspension was introduced into the column using a syringe pump (Harvard Apparatus, Holliston, MA, USA), followed by the introduction of at least 3 PVs of nanoparticle-free brine solution. Column effluent was collected continuously in 15-mL plastic centrifuge tubes (VWR International, West Chester, PA, USA) using a Retriever II fraction collector (Spectrum Chromatography, Houston, TX, USA) and analyzed following the procedures described in Section 2.3. All solutions were delivered at a constant flow rate of 1.0 mL/min, which corresponded to a pore-water velocity of 7.6 m/d. In order to assess the effects of mass loading on nMag-PAMPS-PAA mobility in porous media, two approaches were used: (1) increasing the input concentration from 30 to 1,000 mg/L as the pulse width was maintained at ca. 3 PVs; (2) elevating the pulse width from 0.16 to 3.0 and then to 5.3 PVs while the input concentrations remained at 1,000 mg/L. To investigate the potential for surfactants to enhance nanoparticle mobility, two commercially-available surfactants, Tween[®] 80 (nonionic) and STEOL[®] CS-330 (anionic), both at 1,000 mg/L, were premixed into the nMag influent suspensions prior to introduction into columns. A total of nine column experiments were conducted as summarized in Table 1.

2.3 Analytical Methods

The mean diameter of the nanoparticles were determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS Analyzer (Malvern Instruments, Southborough, MA, USA), operated in non-invasive back scattering (NIBS[®]) mode at an angle of 173°. Approximately 1 mL of nMag-PAMPS-PAA input solution was loaded into a disposable cuvette and analyzed using a red laser at a wavelength of 633 nm.

Col	AMPS/AA	Surfactant	C_0 (mg/L)	PW	d_{NP}	Ret%
#1	1:1	None	27.7	3.2	146.5	99.1
#2	1:1	None	1064	3.2	151.9	8.6
#3	3:1	None	33.7	3.0	110.3	99.0
#4	3:1	None	1064	3.0	119.2	4.0
#5	1:1	None	980.6	0.16	118.7	100
#6	1:1	None	938.0	0.9	114.7	38.8
#7	1:1	None	984	3.1	120.5	10.0
#8	1:1	Tween [®] 80	32.5	5.0	112.5	99.3
#9	3:1	STEOL [®] CS-330	37.0	3.3	108.3	32.0

Note: C_0 – input concentration of nMag-PAMPS-PAA, PW – pulse width, d_{NP} – mean hydrodynamic diameter, Ret% - fraction of retained nMag

Table 1: Experiment matrix and conditions.

All DLS measurements were performed in triplicate, and the accuracy of the system was confirmed using a suspension of monodispersed polystyrene spheres (Nanosphere Size Standards, Duke Scientific, Palo Alto, CA, USA) with a mean diameter of 97 ± 3 nm. To determine the nMag concentration in stock suspension, the nanoparticle stock was diluted by 100-fold with DI water. The Fe content in diluted suspension was quantified using an Optima 7300 DV ICP-OES (Shelton, CT, USA) based upon a five-point calibration curve over a concentration range of 0 to 100 mg/L. For experiments conducted with the input concentration of 1,000 mg/L, concentrations of nMag-PAMPS-PAA in effluent samples were determined using a UV-Vis spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD, USA) scanned over a wavelength range of 500 to 700 nm. The absorbance response at 600 nm was used for quantification based on a five-point calibration curve prepared by serial dilution of nMag-PAMPS-PAA stock suspension. To measure nMag-PAMPS-PAA concentrations in aqueous samples collected in experiments with a 30 mg/L input concentration, an acid-digestion and ferrozine colorimetric method was employed. An aliquot (1.5mL) of effluent sample was digested with 7.8M HNO_3 using a pressurized microwave digestion system (Discover SP-D, CEM Corp. Matthews, NC, USA). The Fe concentration in digested samples was then determined using the ferrozine method [7] and quantified using an UV-Vis spectrophotometer (Shimadzu Scientific Instruments) operated at a wavelength of 562 nm.

3 RESULTS AND DISCUSSIONS

3.1 Transport of nMag at Different Loadings

Relative effluent nMag-PAMPS-PAA concentrations (C/C_0 , where C is measured effluent concentration and C_0 is the influent concentration) were plotted against the number of dimensionless pore volumes of influent solution

introduced into the column. The resulting effluent BTCs obtained for nMag-PAMPS-PAA transport in 40-50 mesh Ottawa sand at two different influent concentrations (30 and 1,000 mg/L) are shown in Figure 1. The area under BTC represents the fraction of nanoparticle mass recovered in the column effluent, and thus, the lower maximum concentration and later breakthrough times are indicative greater interactions between nanoparticles and the porous medium. At the input concentration of 30 mg/L, a 3 PV pulse injection of nMag-PAMPS-PAA resulted in negligible breakthrough, consistent with complete retention of nMag particles in 40-50 Ottawa sand under a brine condition. Increasing the applied nMag concentration by approximately 33-fold led to the recovery of more than 90% of introduced nMag in the column effluent (Table 1). These findings indicate nMag mobility is strongly influenced by the maximum or limiting capacity of the the porous medium (40-50 mesh Ottawa sand) to retain nanoparticles.

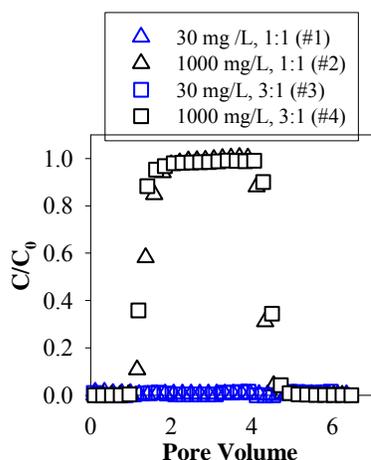


Figure 1. Effluent breakthrough curves of nMag-PAMPS-PAA with AMPS:AA ratios of 1:1 and 3:1 transport in 40-50 mesh Ottawa sand at two different input concentrations (30 and 1,000 mg/L).

To further investigate the role of a maximum retention capacity on the transport and retention of nMag, three more experiments were conducted with varying pulse width at the same input concentration (1,000 mg/L). When a pulse of 0.16 PV nMag-PAMPS-PAA suspension was introduced into the column, complete retention of nanoparticles was observed (Figure 2). An increase of pulse width from 0.16 to 0.9 PV reduced the fraction of retained mass from 100% to 38.8% (Table 1). As the pulse width was further increased to 3.2 PVs, approximately 91.4% of input mass transported through Ottawa sand, yielding a retention of 8.6%. These findings present demonstrated the important role of maximum retention capacity on nanoparticle transport in porous media under these experimental conditions. That is, depending upon the mass of nanoparticles injected into a reservoir formation limited

nanoparticle mobility may be observed until the maximum retention capacity is reached.

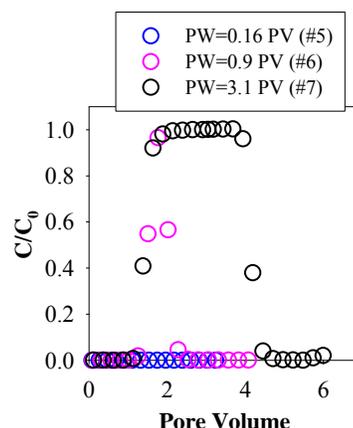


Figure 2. Comparison of nMag-PAMPS-PAA transport in 40-50 mesh Ottawa sand at three different pulse width. The nMag influent concentration was 1,000 mg/L.

3.2 Influence of AMPS:PAA Ratio

The sulfonate functional group in polymer coating is known to exhibit high resistance to bind Ca^{2+} in brine solution. The content of sulfonate in copolymer formulation potentially affects nMag interactions with porous media, and in turn, their nanoparticle mobility. The effluent BTCs of nMag-PAMPS-PAA with two different AMPS:AA ratios and at an influent concentration of 1,000 mg/L are shown in Figure 1. Under current experimental conditions, the retained fraction of nMag increased by a factor 2 when the AMPS:AA ratio decreased from 3:1 to 1:1 (Table 1). These findings suggest that a higher sulfonate group content in the polymer coating enhances nMag mobility, although more studies of nMag transport at higher AMPS:AA ratios are needed to confirm the observed trend.

3.3 Effects of Surfactants on nMag Mobility

The effluent BTCs of nMag-PAMPS-PAA for an input concentration of 30 mg/L, in absence and presence of two surfactants, are shown in Figure 3. As noted previously, injection of a 3 PV pulse of nMag mass resulted in complete retention of the applied nanoparticle mass. The addition of 1,000 mg/L Tween[®] 80 to the influent nMag-PAMPS-PAA suspension resulted in a negligible

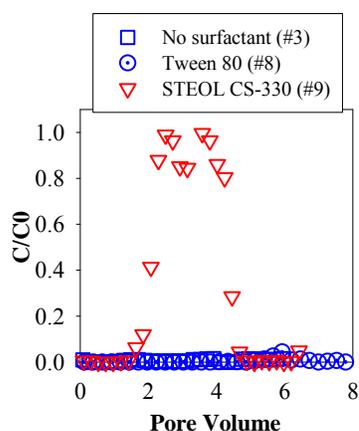


Figure 3. Effluent breakthrough curves of nMag-PAMPS-PAA in absence and presence of premixed nonionic (Tween 80) and anionic (STEOL CS-330) surfactants. The concentrations of nMag and surfactant in input suspensions were 30 and 1,000 mg/L, respectively.

improvement in nanoparticle mobility in the presence of brine (Figure 3). In contrast to Tween[®] 80, the addition of STEOL[®] CS-330 to the input suspension increased the transport of nMag-PAMPS-PAA to over 68% of total input mass, although the nanoparticle breakthrough was slightly delayed. These results demonstrate the potential capacity of anionic surfactants to improve nMag mobility in porous media. The observed enhancement in nMag transport in the presence of anionic surfactant may be due to adsorption of anionic surfactant, which could result in repulsive electrostatic interactions between nanoparticles and solid surfaces.

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