



Retention of silica nanoparticles on calcium carbonate sands immersed in electrolyte solutions



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ABSTRACT

Understanding nanoparticle–surface adhesion is necessary to develop inert tracers for subsurface applications. Here we show that nanoparticles with neutral surface charge may make the best subsurface tracers, and that it may be possible to use SiO₂ nanoparticle retention to measure the fraction of solid surface that has positive charge. We show that silica nanoparticles dispersed in NaCl electrolyte solutions are increasingly retained in calcium carbonate (calcite) sand-packed columns as the solution ionic strength increases, but are not retained if they are injected in pure water or Na₂SO₄ electrolyte solutions. The particles retained in the NaCl experiments are released when the column is flushed with pure water or Na₂SO₄ solution. AFM measurements on calcite immersed in NaCl solutions show the initial repulsion of a silica colloidal probe as the surface is approached is reduced as the solution ionic strength increases, and that at high ionic strengths it disappears entirely and only attraction remains. These AFM measurements and their interpretation with Derjaguin–Landau–Verwey–Overbeek (DLVO) theory shows the calcite surface charge is always negative for Na₂SO₄ solutions, but changes from negative to positive in a patchy fashion as the ionic strength of the NaCl solution increases. Since mixed-charge (patchy) surfaces may be common in the subsurface, nanoparticles with near-zero charge may make the best tracers.

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1. Introduction

Aggregation and deposition of engineered nanomaterials is largely controlled by physicochemical interactions [1]. In drug delivery and in medical diagnosis it is critical that the nanoparticle remain in the blood long enough to reach target organs to be imaged or tumor cells to be treated [2]. The interactions of nanoparticles with biological units controls the formation of nanoparticle clusters on the membranes, and the formation of these clusters improves drug delivery efficiency [3]. The nanofabrication of electronic and optical devices depends on the interaction of nanostructured materials with fabricated devices. These interactions are affected by chemical conditions, and manipulation of these conditions allows the construction of the dyads, triads, strings, clusters, and other architectures that are the basis of a new generation of nano-devices and smart materials [4,5]. The size, shape, and composition of the particles and hydrodynamic conditions are important, but so also is the surface charge of the particles, and this is controlled by the chemistry of the surrounding solution (e.g. pH, ionic strength, and ionic composition) [1,3,5].

Size-dependence of nanoparticle adsorption has been reported for silica [6], gold [7], silver [8,11] and carbon nanotube particles [9]. The optimal size seems to be that which allows the ordered formation of nanoparticle monolayers [10]. The curvature of the surface of the nanoparticle could influence adsorption and the properties of the adsorbed particles [11]. Nanoparticles with different shapes interact differently with the same substrates. Pal et al. showed that antibacterial properties of silver nanoparticles undergo a shape-dependent interaction with bacteria [12].

Solution chemistry is a critical external factor controlling nanoparticle behavior [1,13]. The pH, ionic strength, and the ionic composition of the solution controls nanoparticle stability primarily by changing surface charge. Maintaining the solution within a range of pH and ionic strength is usually required to maintain a stable nanoparticle suspension. The width of the stability range depends on the nanoparticle chemistry and the ions in solution [14,15]. Increasing the ionic strength of a solution increases the nanoparticle retention in silica sand packed column [16,17], and the mix of aqueous ions affects particle retention [18,19]. Many nanoparticles such as silica, polystyrene latex, and TiO₂ have been injected into sand packed laboratory columns and into the subsurface, and it has been found that the mineralogy of the nanoparticle and the solid materials it contacts influence transport behavior

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[20]. Silica nanoparticles are not retained at all when passed through quartz sands and sandstone, but are slightly retained in limestone [1,21]. A slug of water can completely mobilize silica particles retained in a limestone packing [21]. Silica colloids and nanoparticles are the most commonly selected engineered nanomaterials for water treatment and contaminant remediation [22–24], and their behavior in porous rock media has been widely studied.

It has been possible to understand much of this behavior theoretically. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory predicts interfacial forces between a particle and a surface [16]. The interaction force is the sum of the van de Waals (VdW) and electrostatic double layer (EDL) interactions. The VdW forces are of relatively short-range and always present, but are not very sensitive to solution ionic strength. EDL forces are relatively long-range and are sensitive to solution ionic strength. To account for nanoparticle adsorption on organic surfaces, the DLVO theory has been extended to include repulsive steric force [25]. Hydrophilic and hydrophobic forces [26] and even magnetic force [27] can influence nanoparticle aqueous suspensions.

Nanoparticle–surface interaction in aqueous solutions has been investigated at nano scale using techniques such as X-ray diffraction [28], atomic force microscopy (AFM) [29], and quartz crystal microbalance (QCM) [30]. These methods directly measure the interactions of nanoparticles with solid surfaces and their molecular arrangement and ordering [31,32]. Nanoparticle–surface interactions in aqueous solutions have also been studied using columns packed with sands of various mineralogy. But few studies combine these methods, and we still lack a comprehensive and fundamental understanding of what controls particle retention in porous media.

In this paper, we study silica nanoparticle stickiness not only using column methods but also atomic force microscopy measurements and DLVO theory. First the retention of silica nanoparticles in both NaCl and Na₂SO₄ solutions is measured when silica particles dispersed in solution are passed through a calcite sand-packed column. We then make atomic force microscopy measurements between a silica colloidal AFM probe and calcite submerged in similar NaCl and Na₂SO₄ solution. The surface charge on the calcite surface is inferred from the AFM force profiles using the DLVO theory. The surface charge on the calcite is always negative for the Na₂SO₄ solutions and negative in low ionic strength NaCl solutions, but positive in higher ionic strength NaCl solutions. The NaCl column experiments suggest that this transition in surface charge occurs as the proportion of the calcite surface with positive charge increases as the NaCl ionic strength increases. Particles that electrostatically adhere to the areas with positive surface charge in high ionic strength NaCl solution can therefore be released when dilute solution are introduced and these areas of positive charge disappear. Our motivation in this and other studies is to develop non-interacting nanoparticle tracers for subsurface flow applications [33], and this paper follows up on a suggestion that near-zero particle charge (zeta potential) minimized particle retention [34]. The results of the experiments reported here indicates that zero charge nanoparticles may make the best non-reactive tracers because minerals with mixed surface charge will likely be common in the subsurface.

2. Materials and methods

2.1. Materials

2.1.1. SiO₂ nanoparticles

Green fluorescent SiO₂ nanoparticles were purchased from Corpucular Inc. (Cold Spring, NY). The particle diameter was 87 ± 12 nm. The particle morphology and fluorescence spectrum are shown in Fig. S1 (Supporting Information).

2.1.2. Electrolyte solutions

The electrolyte solutions were prepared using analytical grade NaCl (Sigma–Aldrich) and Na₂SO₄ (anhydrous, granular, Mallinckrodt Chemicals) without further purification. The preparations are described in Text S1 (Supporting Information).

2.1.3. Calcite samples

The calcite (calcium carbonate) that was used in AFM measurements was iceland spar (calcite polymorph, Ward's Natural Science). A cold chisel was used to cleave off approximately a 1 cm cube of optically clear calcium carbonate crystal. This provides {10 $\bar{1}$ 4} cleavage surfaces that are atomically flat over several to tens of micrometers, a prerequisite for high-quality AFM measurements [35]. The {10 $\bar{1}$ 4} surfaces contain both Ca and CO₃ ions, making it charge neutral, and has a higher density of ions than other possible neutral planes, leading to its low surface energy and stable surfaces [36]. The sample preparation was done a day before the AFM measurements. The calcite sands that were used to pack the column were purchased from Specialty Mineral Inc., Lucerne Valley, CA. The sands contain 97% calcium carbonate. The average particles size is 300–500 μm.

2.2. Column design and experiments

The column experiments were conducted by passing tracer particle solutions through a transparent polycarbonate column filled with calcium carbonate sands (see Fig. S2, Supporting Information). The design of the column similar with previous column experiments [37] is described in Text S2 (Supporting Information).

A tracer solution is prepared which contains 100 ppm SiO₂ nanoparticles and either 0.5 mM, 10 mM, or 100 mM NaCl (or Na₂SO₄). The nanoparticle/electrolyte solution is pumped slowly into the bottom of the column using a peristaltic pump at a flow rate of 0.3 ml/min for a certain period of time so that a slug of tracer is introduced into the column. This tracer slug is followed by the same NaCl (or Na₂SO₄) solution without SiO₂ nanoparticles. After this, DI water is pumped through the column in some experiments as indicated. Effluent is collected every 4 min. The nanoparticle concentration of the effluent is determined using a previously-determined fluorescence – concentration calibration curve. Fluorescent spectroscopy (SpectroMax M5, Molecular Devices, LLC) is used to determine the relationship between SiO₂ particle concentration and particle fluorescence intensity (515 nm). The ratio of collected to injected particle concentrations is plotted against the pore volume throughput.

2.3. AFM measurements

An atomic force microscope system (NTEGRA Prima, NT-MDT, Zelenograd, Russian Federation) was employed to perform direct force measurements on the calcium carbonate submerged in liquid. Electrolyte (NaCl or Na₂SO₄) solution was added to a stainless steel cell where the calcium carbonate, which was glued to the bottom of the cell, was submerged. A SiO₂ colloidal AFM probe was purchased from Novascan Technologies. An amorphous SiO₂ colloid (5 μm in diameter) was attached on the end of the AFM cantilever, as shown in the SEM image in Fig. S3a (Supporting Information). The SiO₂ colloidal probe was used to directly measure the force between the silica colloid and the calcium carbonate surface as the colloid approached the surface. A 20 μm × 20 μm area of the submerged calcite surface was probed at 36 points by the AFM using the SiO₂ colloidal probe and the results averaged. The same 36 points were probed for all solutions. The geometry of the tip was examined with a scanning electron microscope before and after force measurements. This confirmed that the radius of the tip that contacts the calcite surface was roughly

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