# Transport of colloidal silica in unsaturated sand: Effect of charging properties of sand and silica particles

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## HIGHLIGHTS

- Transport of colloidal silica was examined in unsaturated sand column.
- Amount of silica deposition depends on solution pH even in unsaturated condition.
- Water contents were less effective on deposition amount at high pH condition.
- Water contents significantly affect deposition amount at low pH condition.

## ARTICLE INFO

## ABSTRACT

We have studied the transport of colloidal silica in various degrees of a water-saturated Toyoura sand column, because silica particles are widely used as catalyst carriers and abrasive agents, and their toxicity is reported recently. Since water-silica, water-sand, and air-water interfaces have pH-dependent negative charges, the magnitude of surface charge was controlled by changing the solution pH.

The results show that, at high pH conditions (pH 7.4), the deposition of colloidal silica to the sand surface is interrupted and the silica concentration at the column outlet immediately reaches the input concentration in saturated conditions. In addition, the relative concentration of silica at the column outlet only slightly decreases to 0.9 with decreasing degrees of water saturation to 38%, because silica particles are trapped in straining regions in the soil pore and air-water interface.

On the other hand, at pH 5 conditions (low pH), where sand and colloid have less charge, reduced repulsive forces result in colloidal silica attaching onto the sand in saturated conditions. The deposition amount of silica particles remarkably increases with decreasing degrees of water saturation to 37%, which is explained by more particles being retained in the sand column associated with the air-water interface.

In conclusion, at higher pH, the mobility of silica particles is high, and the air-water interface is inactive for the deposition of silica. On the other hand, at low pH, the deposition amount increases with decreasing water saturation, and the particle transport is inhibited.

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## 1. Introduction

Over the past two decades, research has discussed how contaminants adsorbed on colloidal particles, such as clay mineral, metal oxides and microorganisms, migrate with particles (McCathy and Zachara, 1989; Novikov et al., 2006). In addition, with the growth of the nanoparticle industry, it has been pointed out that engineered nanoparticles act as harmful contaminants in the vadose zone and aquifer (Maynard et al., 2006).

Oxide nanoparticles such as silica and titania, which seem to be less harmful, are also potentially toxic (Yamashita et al., 2011). Therefore, it is necessary to understand the fate of oxide nanoparticles for appropriate management of subsurface environments from the two aspects of carriers and harmful contaminants.

Silica particles are particularly used widely in many industries as catalyst carriers and abrasive agents. Furthermore, silica coating is used for the improvement of the dispersibility of engineered nanoparticles (Guerrero-Martínez et al., 2010). High dispersibility leads to high mobility in environmental conditions. Furthermore, recent research shows that some radioactive contaminants from

the Fukushima Daiichi Nuclear Power Plant accident were released as spherical microparticles of silicate glass (Yamaguchi et al., 2016). Therefore, we should pay attention to the transport of silica and silica-coated particles in the vadose zone.

Colloidal particles are generally transported through water flow with a fraction of particles being deposited onto the soil matrix surface. To understand the colloid transport phenomenon, we need to evaluate the rate of colloid deposition to the soil matrix. Colloid deposition is generally assumed to occur in two limiting steps. The first step is the transport of particles to the soil surface; the second step is the attachment of transported colloidal particles to the matrix surface. Within these two steps, attachment largely depends on interaction forces between the soil matrix and colloidal particles (Kretzschmar et al., 1999). Two major interaction forces are the van der Waals force and the electric double layer force. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, colloid attachment is evaluated by the summation of the attractive van der Waals force and repulsive electric double layer force. The magnitude of the electric repulsive force depends on solution pH, ionic strength, and ionic species. Therefore, chemical solutions play an integral role and have been an important part of research on colloid and nanoparticle transport (Johnson and Elimelech, 1995; Elimelech and O'Melia, 1990; Ryan and Elimelech, 1996; Kobayashi et al., 2009; Sagee et al., 2012; Hotze et al., 2010).

Furthermore, particle aggregation should be considered when attempting to understand transport behavior, as particle aggregation induces changes in particle size. As a result, the deposition rate of particles changes over time (Raychoudhury et al., 2010, 2012; Phenrat et al., 2009; Petosa et al., 2010; Chan and Vikesland, 2014). Even in solution conditions unfavorable for deposition, aggregated particles are removed by the straining effect (Chowdhury et al., 2011).

Previous studies, however, that focused on interaction forces and particle aggregation, have been carried out mainly in water-saturated conditions. In many actual cases, particles must pass through the vadose zone to reach the aquifer. Thus transport and interaction should be considered, even in unsaturated conditions. In unsaturated porous media, colloidal particles can be retained not only at the solid-water interface but also at the air-water interface, in flow stagnation regions, and at air-water-solid interfaces. Therefore, the amount of colloid deposition generally increases and deposition mechanisms become complex under unsaturated conditions (Wan et al., 1994; Lenhart and Saiers, 2002; Saiers and Lenhart, 2003a; Bradford and Torkzaban, 2008). Also, even in unsaturated condition, colloid deposition depends on interaction forces in addition to the degree of water saturation. For example, the deposition amount of colloidal particles to the air-water interface increases with increasing solution ionic strength due to the diminishing electric repulsive forces between colloidal particles and the air-water interface (Saiers and Lenhart, 2003b; Torkzaban et al., 2006b). Furthermore, the trapping of particles in the flow stagnation region is also affected by the solution ionic strength (Torkzaban and Bradford, 2008). In contrast to the studies examining the effect of ionic strength, there are fewer studies concerned about the charging properties of colloidal particles and the soil matrix. Nevertheless such factors are also believed to control the electric interaction force and change colloid deposition behavior in unsaturated conditions.

According to Wan et al. because the air-water interface has a negative charge, positively charged particles can become trapped there (Wan and Tokunaga, 2002; Li and Somasundaran, 1991). Torkzaban et al. performed experiments on the transport of two kinds of viruses where surface potentials are controlled by solution pH, in both saturated and unsaturated sand columns. Both virus types have different isoelectric points (iep); one is pH 3.9 and the

other is pH 6.7. The deposition amount of the virus with the higher iep increased with decreasing pH; this was due to the surface potential of the virus reversing to positive in low pH conditions. The researchers also showed that the deposition amount of the virus with an iep of 6.7 increased with decreasing water content at pH 5.5 conditions. This can be explained as positively charged viruses with an iep of 6.7 are easily trapped at a negatively charged air-water interface (Torkzaban et al., 2006a). Gao et al. also studied the effect of pH-dependent charges using two different types of clay minerals: kaolinite and illite. Both minerals showed a zeta potential between $-40$ mV and $-30$ mV in the pH range of 4.6—7.4. However, the edge surfaces of the clay particles were positively charged at a lower pH. In saturated conditions, transport behavior of clay was less affected by clay species and solution pH. Under unsaturated conditions, however, the deposition amount of kaolinite significantly increased when the solution pH was 4.6. The researchers concluded that positively charged edge surfaces tend to attach to the air-water interface (Gao et al., 2004). Due to difficulties stemming from the heterogeneous natures of viruses and clays, it is difficult to further discuss the effect of charge on colloid transport. The effect of a partial positive charge is unclear; nevertheless, charge properties significantly influence depositions in unsaturated porous media.

Meanwhile, some studies suggest there are different mechanisms for deposition to the air-water interface. Chen et al. for example, investigated the transport of three kinds of negatively charged latex particles, which had different surface charge densities but the same diameters in unsaturated silica sand columns. The deposition amount of all three kinds of latex particles increased with decreasing degree of water saturation. Particles with high charge density, however, were more easily trapped in the column. The researchers suggested that the large repulsive force between colloidal particles and the air-water interface promoted colloid attachment to the solid surface by overcoming energy barriers between the sand surface and colloidal particles (Chen et al., 2007; Chen and Flury, 2005). These results imply that the surface charge of the air-water interface and the solid-water interface should be considered when evaluating the interaction and deposition. However, these studies did not sufficiently pay attention to charge properties of the soil matrix. They only controlled the charge amount of colloidal particles and neglected charge properties of sand and the air-water interface.

In terms of industrial applications, charge properties of colloidal particles and air bubbles have been well studied, resulting in reliable available data (Bolt, 1957; Kobayashi et al., 2005a; Yang et al., 2001; Najafi et al., 2007). Few studies, however, focus on charge properties of the soil matrix. The charge properties of the soil matrix should be considered as well as colloidal particles and the air-water interface in order to better understand colloid transport in unsaturated conditions. Therefore, in this study, we conducted column experiments by using well-characterized materials to clarify the effect of charge properties on colloid transport in porous media with varied water content. We aim to show fundamental transport behaviors of silica particles in unsaturated conditions.

## 2. Materials and methods

### 2.1. Colloids

Submicron colloidal silica (KE-P10 LOT: 1B18, Nippon Shokubai) was used as the colloidal particles. Silica particles were heated at 800 °C over 24 h, and dispersed in water (Kobayashi et al., 2005b). The silica was characterized by transmission electron microscopy, specific surface area with $N_2$-BET and zeta potential. The silica particles were of spherical shape and uniform in size, with an