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# Transport of silver nanoparticles in single fractured sandstone

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ABSTRACT

Silver nanoparticles (Ag-NP) are used in various consumer products and are one of the most prevalent metallic nanoparticle in commodities and are released into the environment. Transport behavior of Ag-NP in groundwater is one important aspect for the assessment of environmental impact and protection of drinking water resources in particular. Ag-NP transport processes in saturated single-fractured sandstones using triaxial flow cell experiments with different kind of sandstones is investigated. Ag-NP concentration and size are analyzed using flow field-flow fractionation and coupled SEM-EDX analysis. Results indicate that Ag-NP are more mobile and show generally lower attachment on rock surface compared to experiments in undisturbed sandstone matrix and partially fractured sandstones. Ag-NP transport is controlled by the characteristics of matrix porosity, time depending blocking of attachment sites and solute chemistry. Where Ag-NP attachment occur, it is heterogeneously distributed on the fracture surface.

## 1. Introduction

Silver nanoparticles (Ag-NP) are used in various consumer products and are one of the most prevalent metallic nanoparticle in commodities (Nowack et al., 2012; Klaine et al., 2008). Ag-NP are released from many of these goods (Geranio et al., 2009; Benn and Westerhoff, 2008; Kaegi et al., 2011; Hagendorfer et al., 2010) and their fate in the environment is of major interest (Meier et al., 2016; Pradas del Real et al., 2016; Garg et al., 2016). In this context, transport behavior of Ag-NP in groundwater is one important aspect for the assessment of environmental impact and protection of vital drinking water resources in particular.

Studies on transport of engineered nanoparticles (ENP) in water saturated and partly saturated porous media are numerous (e.g. Fang et al., 2009; Jaisi and Elimelech, 2009; Kasel et al., 2013; Liang et al. 2013; Wang et al., 2012). Mobility of ENP is controlled by its physicochemical properties, the porous medium, solution chemistry and hydrodynamic conditions of the system. Idealized systems, such as glass beads and quartz sand (e.g. Kasel et al., 2013; Liang et al. 2013; Lin et al., 2011; Taghavy et al., 2013) as well as natural porous media systems have been considered in transport studies (e.g. Cornelis et al., 2013; Fang et al., 2009; Sagee et al., 2012; Kasel et al., 2013). Results show that transport of ENP in natural porous media is much more complex than in idealized systems, due to heterogeneity of porous media surface and cation exchange processes.

Several investigations under idealized experimental conditions have shown the sensitivity of Ag-NP transport to physicochemical parameters promoting aggregation and deposition processes, due to the compression of the electrostatic double layer and decrease of repulsive interaction (Liang et al., 2013a; Lin et al., 2011; Thio et al., 2012). The relevance of physicochemical properties may be masked by the presence of stabilizing agents that enhance repulsion between Ag-NP particles as well as between Ag-NP and porous media surface resulting in greater mobility of Ag-NP. In addition, Ag-NP transport depends on grain and pore size of the porous media, and fluid flow velocities (Liang et al., 2013a; Sagee et al., 2012; Neukum et al., 2014a; Taghavy et al., 2013).

At conditions unfavorable for Ag-NP attachment, physicochemical filtration is controlled by heterogeneity of the collector surface with local favorable attachment sites (Lin et al., 2011). Transport of Ag-NP in natural porous media is associated with blocking of attachment sites and subsequent time-dependent increase in Ag-NP transport. Time-dependent attachment of Ag-NP is reported for quartz sand (Liang et al., 2013a; Braun et al., 2015), natural loamy sand (Liang et al., 2013b; Braun et al., 2015), porous unfractured sandstone matrix (Neukum et al., 2014a), and partially fractured sandstone (Neukum et al., 2014b). Increase of Ag-NP retention with increasing clay mineral content is associated with positively charged crystal edges (Cornelis et al., 2013). Colloid-facilitated transport of Ag-NP is reported for natural loamy sand, due to cation exchange and subsequent release of clay minerals (Liang et al., 2013b) and partially fractured sandstone (Neukum et al., 2014b). Unsaturated flow conditions influencing particle interaction at biogeochemical interfaces (Kumahor et al., 2016).

Only a few studies on Ag-NP transport in consolidated rocks are

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published to date. Neukum et al. (2014a) studied Ag-NP transport in three different unfractured sandstones. The same sandstone types are used in experiments under partially fractured conditions (Neukum et al., 2014b). Physicochemical filtration, straining, time-depending blocking of attachment sites and colloid-facilitated transport were identified as major transport processes of Ag-NP mobility. Physicochemical filtration depends on solute chemistry, mineralogy, pore size distribution, and probably on physical and chemical heterogeneity of the Ag-NP-rock system. Ag-NP mobility in unfractured sandstone matrix reduces with decreasing mean pore size, decreasing hydraulic conductivity and the presence of metal-oxides/hydroxides. Partial fracturing of the sandstone matrix increases Ag-NP mobility, due to larger void space and higher hydraulic conductivity.

Residence time of colloids in parallel-plate fractures, compared to solute resident time, depends on the ratio of colloid radius and aperture width of the parallel-plate fracture. The velocity distribution assumption (size-exclusion) states that colloid retention time decreases with increasing ratio of colloid radius and fracture aperture (Zheng et al., 2009). Colloids are known to diffuse hardly into rock matrix, due to their size. In a sensitivity analysis related to the colloidal matrix diffusion in discretely fractured porous media, the upper boundary of the colloid size that can diffuse into the matrix is 1.0 µm (Oswald and Ibaraki, 2001). Under unfavorable electrostatic conditions gold, latex and smectite colloids travel as fast as or faster than water in an artificially fractured crystalline rock. Colloid size, mean water velocity, and fracture aperture are identified to control the transport velocity of colloids (Albarran et al., 2013). Colloid mobility in fractures is influenced by colloid size and surface roughness variations. Large colloids (1000 nm) undergo sedimentation in stop-flow mode and collector interaction is not affected by surface roughness variations. For small colloids (25 nm), sedimentation is not an important process, but surface inhomogeneity triggers collector interactions (Stoll et al., 2016). Kim et al. (2015) investigated latex colloid transport in fractured media and concluded that mobility of these colloids are mainly influenced by filtration than by colloid velocity.

Transport of Ag-NP in three different single-fractured sandstones is investigated in column experiments, where different fluid chemistries are applied. Transport in unfractured and partially fractured sandstone depends, among others, on solute chemistry, and time dependent attachment is identified as one major transport process. These processes are investigated in this study with single-fractured sandstones using the same types of sandstone as in our former experiments (Neukum et al., 2014a; Neukum et al., 2014b) to assure comparability in terms of mineralogy and matrix pore size distribution. Ag-NP concentration and size are analyzed by flow field-flow fractionation. We identify the main transport processes of Ag-NP in fractured sandstones based on our experimental results and discuss the environmental implications of these results to Ag-NP mobility in fractured groundwater resources.

## 2. Materials and methods

### 2.1. Rock characteristics

Three different sandstone types are used in this study: The Pliocene Herzogenrather (S4), the Cretaceous (Berrias) Obernkirchner (S14) and the Triassic Solling (S10) sandstones. S14 and S10 represent important fractured aquifers, which are used for water supply in Germany. All of the sandstone types have been already tested for Ag-NP transport through the rock matrix and partially fractured systems (Neukum et al., 2014a, 2014b). The sandstones differ in mineralogy and pore size distribution. Detailed information is published elsewhere (Fitzner and Kownatzki, 1991; Neukum et al., 2014a). The main characteristics are briefly summarized in Table 1.

**Table 1**
Composition and characteristics of the sandstone samples according to Fitzner and Kownatzki (1991) and Neukum et al. (2014a).

| | S4 | S10 | S14 |
|---|---|---|---|
| Quartz (%) | 95 | 53 | 82.4 |
| Feldspar (%) | | 14.1 | 1.6 |
| Lithic fragments (%) | 5 | 5.4 | 3.8 |
| Clay minerals (%) | | 6.4 (chlorite) | 10.4 (kaolinite) |
| Iron oxides/hydroxide (%) | | 14.2 | 0.2 |
| Carbonate (%) | | 3.2 | |
| Micas (coarse-grained) (%) | | 2.3 | 0.8 |
| Heavy minerals (%) | Accessory | 0.5 | 0.5 |
| Opaque substances (%) | | 0.9 | 0.3 |
| Density (g/cm$^3$) | 2.1 | 2.34 | 2.18 |
| Average grain size (mm) | ~2.1 | 0.12 | 0.1 |
| Porosity (%) | ~23–26 | ~12 | ~18 |
| Average pore radius (µm) | 21.5 | 0.3 | 3.8 |
| Zeta potential with deionized water (mV) | − 55 ± 0.76 | − 20 ± 1 | − 41.1 ± 2.8 |
| Hydraulic conductivity, matrix (m/s) | $4.5{\cdot}10^{-6}$ | $2.2{\cdot}10^{-10}$ | $2.8{\cdot}10^{-9}$ |

For S10 and S14 straining is anticipated, due to the pore volume fractions smaller than Ag-NP size (20% for S10 and 7% for S14) and to steric hindrance.

### 2.2. Sample preparation and transport experiments

Cylindrical samples of 10 cm length and 5 cm diameter are cut along the major axis in the centre of the column into two pieces to create a single fracture system. The fracture walls are polished with a carbide abradant with subsequent sonication to clean the surfaces and the adjacent pores from saw residues. Both pieces are packed in a triaxial flow cell equipped with filter material (Poroplast Type 162, Durst Filtertechnik, Germany) on top and bottom of the rock samples in order to get uniform fluid flow over the entire cross section of the samples (Fig. 1). A latex rubber sleeve of 5 cm diameter separates the surrounding water pressure from the rock samples. The samples are hydraulically characterized by flow measurements at defined boundary conditions in up-flow mode.

A non-reactive tracer experiment is conducted prior to the Ag-NP transport experiments in each rock sample by injecting a solute concentration of 5 g $L^{-1}$ sodium nitrate for 90 min. The samples are subsequently flushed using deionized water until steady-state solute concentration is achieved, corresponding to an electrical conductivity of the fluid to less than 100 µS $cm^{-1}$. A constant flow rate is established using a high-pressure multichannel dispenser (ICP, ISMATEC, Germany). The breakthrough curves gained with the solute tracer experiments are inversely fitted using the analytical advection-dispersion equation implemented in CXTFIT (Toride et al., 1995). Fitting parameters are solute velocity and dispersion coefficient. The equivalent fracture aperture is calculated using the measured volumetric flow rate and the inversely fitted solute velocity.

The Reynolds number *Re* for each experimental setup is calculated using the fracture apertures following the equation (e.g. Brush and Thomson, 2003; Koyama et al., 2008):

$$Re = \frac{\rho_f Q}{\mu\, b}$$

$\rho_f$: fluid density [$ML^{-3}$]
Q: measured volumetric flow rate [$L^3 T^{-1}$]
µ: dynamic viscosity [$L^{-1}MT^{-1}$]
b: fracture aperture [L]

For the Ag-NP transport experiments, the pore fluid of the rock samples was conditioned to the desired electrolyte solution. Three different solutions were used: deionized water, 1 mM, and 10 mM sodium nitrate. The applied Ag-NP concentration and flow rate were kept

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