

Transport and Deposition Behavior of PEG-Modified Gold Nanoparticles in Natural Barriers

*Carlos Ordonez¹, Shingo Tanaka², Naoko Watanabe² and Tamotsu Kozaki²

¹Graduate School of Engineering, Hokkaido Univ., ²Faculty of Engineering Hokkaido Univ.

Identifying the role and potential influence of colloids in radionuclide transport is important for the performance assessment of high-level waste (HLW) repositories. Thus, to understand the mechanisms governing colloidal transport, deposition experiments with gold nanoparticles (AuNPs) modified with poly (ethylene glycol) (PEG) in porous media were carried out. The deposition behavior was monitored by electron microscopy and our findings confirmed that the transport and deposition behavior is influenced by the PEG-layer stabilizing effects.

Keywords: radioactive waste disposal, natural barriers, gold nanoparticles, transport, aggregation

1. Introduction

Mobile colloidal particles in subsurface environments may act as carriers of sorbing radionuclides and thereby facilitate the transport of radionuclides. Thus, for the development of reliable transport models necessary for the safety assessment of HLW deep geological repositories, understanding colloidal transport mechanisms is crucial. In our previous reports [1, 2], we have used PEG-coated AuNPs with different sizes in column and batch experiments as a representative colloid to understand their transport and deposition behavior as well as the mechanisms involved. Through optical spectral properties studies, we proposed that the interactions between the AuNPs and the silica sand grains caused the observed AuNPs retention and aggregation. In this work, electron microscopy was used to observe the distribution of AuNPs attached onto silica sand surfaces to understand the interactions occurring between them and their influence in their deposition behavior.

2. Materials and Methods

Negatively charged AuNPs (NanoComposix, USA) with three different Au-core diameters (10, 50 and 100 nm) and coated with thiol PEG polymeric units ($M_w \sim 5$ kDa) were used in batch deposition experiments in silica sand grains. Samples were prepared by mixing 0.1 g of silica sand with 10 mL of AuNPs aqueous dispersions (12.75, 13.5 and 13 mg/mL for 10, 50 and 100 nm respectively) in centrifuge tubes for 1 hr at room temperature. The supernatant solutions were removed, the sand grains were vacuum dried and prepared for scanning electron microscopy (SEM) analysis. Randomly selected sand grains were attached to brass stubs using carbon tape and sputter-coating them with a carbon layer. Finally, the sand grains surfaces were thoroughly examined to observe the morphology of the silica sand grains and the deposition behavior of the AuNPs.

3. Result and Discussion

Obtained SEM images for the deposition of AuNPs as well as their distribution onto silica sand grains are shown (Fig. 1). We were able to find a very small amount of dispersed 10 nm AuNPs (Fig. 1a) on a singular location of single sand grain.

However, larger amounts of attached AuNPs with sizes of 50 and 100 nm were easily observed (Fig. 1b, c) in particular locations of several sand grains. These observations are in good agreement with our previous reports [1, 2] where the AuNPs retention in batch and column experiments was negligible for 10 nm and larger for 50 and 100 nm. Furthermore, 10 nm AuNPs were found to be dispersed and sparsely scattered on a smooth depression region of one particular grain, and aggregation was not detected. On the other hand, 50 and 100 nm AuNPs were detected as individual particles as well as aggregates or clusters (arrows in Fig. 1b, c). The aggregation behavior described by the SEM image analysis agrees well with our previous study [1, 2], where temporal evolution analysis of the UV-vis spectra suggested that aggregation within the column porespace occurred. The current study provides evidence and supports the previously proposed transport and deposition mechanism [1, 2], where AuNPs functionalized with short PEG chain lengths (lower stabilization) attach to the positive surface charge heterogeneities (potentially due to accessory minerals) existing on the negative surfaces of the silica sand (cracks and fractures) due to their proximity to the silica sand surfaces. As AuNPs deposits onto the silica sand surface, incoming AuNPs are more likely to interact with deposited AuNPs rather than with the silica sand surface (process known as ripening) due to a charge reversal process, acting as additional collectors. As this ripening process progresses, aggregates are formed in the porespace until eventually detach and elute out of the column or may be retained by straining or physical blocking.

References

- [1] Ordonez, C., Tanaka, S., Watanabe, N. and Kozaki, T.; **2018**, AESJ Spring Meeting, Osaka, Japan.
- [2] Ordonez, C., Tanaka, S., Watanabe, N. and Kozaki, T.; **2017**, AESJ Fall Meeting, Sapporo, Japan.

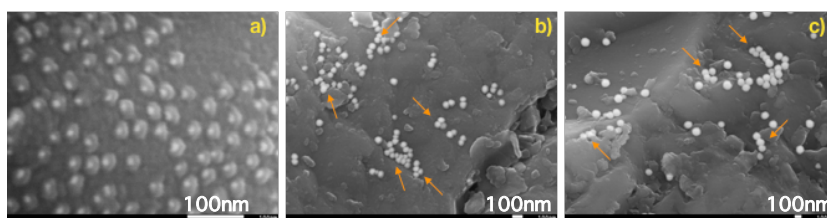


Figure 1. High magnification SEM images of silica sand surfaces showing the deposition behavior of 10 nm (a), 50 nm (b) and 100 nm (c) AuNPs.