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Application of Gold Nanoparticles as Representative Colloids to Understand Environmental Fate and Behavior in Barrier Materials Relevant to Radioactive Waste Disposal

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor in Engineering

by

Carlos Eduardo Ordonez Castillo

Division of Energy and Environmental Systems
Graduate School of Engineering
Hokkaido University
Acknowledgments

Para mi mami hasta el cielo, Flor (Andres, Pablo y Samuel) Andres y Albert quienes me dieron todo su apoyo y consejos durante este viaje, los amo.

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Abstract

Studies on environmental fate and transport of colloidal materials through engineered and natural barriers are highly important for the safety assessment of radioactive waste repositories since the migration behaviors of radionuclides may be significantly affected by interactions with colloids. Synthesized gold nanoparticles of various sizes and surface properties can be used as model colloidal materials to study their migration behaviors in barrier systems to understand the effects of the properties of colloids on their migration behaviors. In this study, gold nanoparticles (AuNPs) of three different sizes (10 nm, 50 nm, and 100 nm) coated with polyethylene glycol (PEG) were used to study the interactions with and migration behavior in silica sand. In addition, interactions of AuNPs with montmorillonite, a typical engineered barrier material to be used in geological disposal, were investigated. The results suggest that there are cases that neither electrostatic nor van der Waals (vdW) interactions control the migration behavior of AuNPs, and other interactions including steric effects arising from the surface coating need to be considered when assessing fate and transport of nanoparticles.

The need for proper radioactive waste management is reviewed as background, including the concepts for near-surface and deep geological repositories of radioactive waste, with an emphasis on the importance of colloid mediated transport in safety assessment. Colloids are defined, and their origins are presented as well as their interaction behavior and the available mathematical models that try to explain them. The complexities and limitations for evaluating natural systems and colloids limit the understanding of the impact of colloid mediated transport. Thus, the potential application of AuNPs as representative natural colloids is proposed, their synthesis, properties and their surface functionalization are presented. The unique size and physicochemical properties found in AuNPs allows an easy characterization and detection that can enhance the current understanding of the interactions between colloidal materials and geomedia that can influence colloidal migration.

Transport experiments using three different sizes of PEG coated AuNPs were carried out in a porous media composed of silica sand to obtain breakthrough curves. The model AuNPs were
characterized by size (in solution and dry), surface charge, surface coating length and optical properties (absorption spectra). The silica sand was used as porous media, and was also characterized in size, morphology and chemical composition. Batch experiments were carried out to understand the colloidal stability of AuNPs and interactions with silica sand. The absorbance spectra of each AuNPs were used to monitor changes in the concentration and in the properties of the AuNPs including aggregation. The transport of AuNPs was observed to be increased for the smaller nanoparticles, and the batch experiments showed that the smaller particles exhibit increased stability against aggregation, although DLVO theory predicts more mobility and stability for larger particles. These results suggest interactions other than electrostatic and vdW, including steric effects provided by the PEG coating, may control the transport behavior in porous media.

The interactions of PEG-coated AuNPs of three different sizes with silica sand grains were studied with more detail. AuNPs were deposited onto silica sand grains in batch experiments, and samples were randomly extracted, vacuum dried and prepared for SEM imaging by coating them with carbon. Elemental mapping was performed to confirm the local chemical composition of the silica sand in order to relate it to the presence of AuNPs. The attachment behavior of the AuNPs observed in the SEM images were consistent with the results from the column transport experiments that showed aggregation observed by the absorption spectra of the column effluent, which may have caused the increased retention of AuNPs in the column. The deposition of AuNPs was observed to be more frequent in the rough surfaces of the silica sand particles. Surface heterogeneities caused by accessory minerals may interact electrostatically with the AuNPs to produce deposition and aggregation. A transport mechanism for the different AuNPs was proposed based on the results of the transport and batch experimental results.

Colloidal interactions between different sized PEG-coated AuNPs and Na-montmorillonite were studied in batch experiments with varying AuNP concentrations. The experiments were conducted at low pH, where stronger interactions between AuNPs and clay edges were expected. The attachment and/or deposition behavior of different AuNPs on Na-montmorillonite particles were examined by UV-Vis, TEM, SEM and EDS. The results
obtained from the absorption spectra showed that possible interactions between the AuNPs and Na-montmorillonite particles. The results of SEM observations showed that no preferential attachment of AuNPs on to edges or surface of Na-montmorillonite, contradicting the expectation of preferential attachment on the edges due to the attractive interactions with the AuNPs. This also suggests a possibility of alternative interactions that may control and modify the attachment behavior of the AuNPs, such as steric effects.

The results of this work provide insights into how the surface properties of colloids impact interactions between colloidal material and barrier materials, thus determining the mobility of colloidal material in engineered and natural barriers. These findings will be an important component in enhancing confidence in the quality of the safety assessment of the HLW repositories.
List of Acronyms and Abbreviations

1D-ADE: 1D advection dispersion equation
AuNP10: gold nanoparticle 10 nm
AuNP100: gold nanoparticle 100 nm
AuNP50: gold nanoparticle 50 nm
AuNPs: gold nanoparticles
BTC: breakthrough curve
CFT: colloid filtration theory
CL: clearance level
DI: deionized water
DLS: dynamic light scattering
DLVO: Derjaguin, Landau, Verwey, and Overbeek
EDL: electrostatic double layer
EDS: energy-dispersive X-ray spectroscopy
ELS: electrophoretic light scattering
HLW: high level waste
HPLC: high performance liquid chromatography
HTO: tritiated water
IS: ionic strength
LLW: low level waste
LSPR: localized surface plasmon resonance
NOM: natural organic matter
NPP: nuclear power plant
NPs: nanoparticles
PEG: polyethylene glycol
PV: pore volume
PZC: point of zero charge
SEI: secondary electron image
SEM: scanning electron microscope
TEM: transmission electron microscope
TOT: tetrahedral-octahedral-tetrahedral
TRU-waste: transuranic waste
UV-Vis: ultraviolet–visible spectroscopy
vdW: van der Waals
XDLVO: extended Derjaguin, Landau, Verwey, and Overbeek
Γ: grafting density
μPIXE: micro particle induced X-ray emission
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Chapter 1. Introduction
1.1 Radioactive Waste Production from Nuclear Power Generation

The rapid development and industrialization of many countries require a long-term, stable, cost effective, and safe supply of energy that can attain low impacts on the environment [1]. Nuclear power is a highly reliable and efficient source of energy with the benefits of low CO$_2$ emission, and consequently an increasing number of countries utilize it to generate electricity. Recent reports showed that around 10% of the world’s electricity is generated by nuclear power reactors (Figure 1.1) and twelve countries produced at least 25% of their internal electricity production from nuclear source and is expected to continue increasing [1].

![World Electricity Production by Source (2018) modified after IAEA (2018)](image)

**Figure 1.1. World Electricity Production by Source (2018) modified after IAEA (2018)**

However, increasing amounts of the radioactive waste generated from the still growing number of nuclear power plants (NPP) around the world has been a great concern [2]. Radioactive waste is a very dangerous type of waste because it can contain significant amounts of radioactive material. The generation of electricity produces large amounts of radioactive waste as a byproduct at different stages of operation such as during mining, fuel enrichment, as spent fuel and/or from plants decommissioning or from accidents. In order to achieve a correct management of radioactive waste, its classification is necessary to ensure that any future handling and/or treatment will be according to the type, volume and risks of the radioactive waste involved. In different regions and/or countries different classifications have been made.
considering that radioactive waste can have different levels of radioactivity and different types of radioactive material can be contained, and in Japan the waste has been classified by their method of disposal while taking into account the methods for its treatment and disposal [3].

1.1.1 Radioactive Waste Classification in Japan

Radioactive waste arising from various activities involved in the generation of electricity needs to be managed safely and properly in order to protect people and the environment [3]. In Japan, radioactive waste is classified into two categories, low-level waste (LLW) and high-level waste (HLW) [3, 4] as shown in Table 1.1. Both HLW and LLW need to be treated, conditioned, stored, and disposed of properly [4]. LLW is generated from operation of NPP and from decommissioning of nuclear facilities. In addition, research and medical activities also generates LLW.

Table 1.1 Classification of Radioactive Waste in Japan modified from JAEA [4]

<table>
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<tr>
<th>Classification</th>
<th>Examples</th>
<th>Origin of Waste</th>
<th>Treatment Method (example)</th>
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<tr>
<td>High-Level Radioactive Waste (HLW)</td>
<td>Canister</td>
<td>Reprocessing Facilities</td>
<td>Geological Disposal</td>
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<tr>
<td>Waste from Power Reactors</td>
<td>Relatively High Radioactive Waste</td>
<td>Control Rods Core Internals</td>
<td>Sub-surface Disposal</td>
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<tr>
<td>HIGH</td>
<td>Liquid Waste Filters</td>
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<td>Near-surface Disposal (Concrete Pit Type)</td>
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<tr>
<td>Radioactive Level ↓ LOW</td>
<td>Used Equipment Expendables</td>
<td></td>
<td></td>
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<tr>
<td>Very Low-Level Radioactive Waste</td>
<td>Concrete Metals</td>
<td>Near-surface Disposal (Trench Type)</td>
<td></td>
</tr>
</tbody>
</table>
LLW is further classified into four categories based on radioactivity concentration and its origin: very low-level radioactive waste, relatively low-level radioactive waste, relatively high-level radioactive waste, and transuranic waste (TRU) shown in Figure 1.2. LLW can contain radionuclides with long half-lives such as Carbon-14 (C-14), Iodine-129 (I-129) [5]. Transuranic elements including Am and several isotopes of Pu also have very long half-lives. Waste below the clearance level (CL) can be released from the regulatory control, which can be handled and disposed/or reused as general non-radioactive waste [4].

**Figure 1.2. Definition of TRU-Waste in Japan modified after JAEA/FEPC (2007) [5]**

Radionuclide concentration of TRU-Waste in Japan and comparison with NPP wastes (green and yellow).
HLW is generated from reprocessing of spent nuclear fuel. In reprocessing, uranium and plutonium are recovered from spent fuel, and liquid high-level waste is generated, which contains fission products and transuranic elements generated in the reactor core. Any liquid high-level waste is vitrified to make HLW.

1.1.2 Strategies for Radioactive Waste Disposal in Japan

Radioactive waste in each category is, or will be, disposed of in different types of disposal facilities depending on the radioactivity levels [6] as shown in Table 1.1. There are three types of disposal facilities for LLW corresponding to each type of LLW. The trench type of near-surface disposal facility, which has shallow trenches without lining, is used for very low-level radioactive wastes (Figure 1.3, left). Another type of near-surface disposal facility is the concrete pit type and is used for relatively low-level waste. The disposal facility has concrete pits, and after the designed quantity of waste is placed, mortar is poured in the spaces between the waste packages, and the facility is covered and enclosed with low water permeability soil to avoid leaching (Figure 1.3, top right). Relatively high-level waste will be placed in intermediate-depth disposal facilities at a depth greater than 70 m below the ground level (Figure 1.3, bottom right).

![Figure 1.3. LLW Disposal Strategies: Trench, Concrete Pit and Intermediate-Depth Disposal modified from JAEA/FEPC (2007) [5].](image-url)
Deep geological disposal facilities are intended for disposal of HLW [6] and some TRU [5]. In Japan, HLW disposal facilities will be constructed in a stable host rock at a depth greater than 300 m [6] (Figure 1.4, right). Geological disposal is considered to provide reliable, safe, and long-term isolation of radionuclides from the biosphere through multi-barrier systems [7-8] (Figure 1.4, left). Multi-barrier systems consist of an engineered barrier system and a natural barrier system (Figure 1.4, left), and are expected to contain the waste for many years [9]. The engineered barrier includes the vitrified waste, metal overpacks, and the bentonite buffer, and the natural barrier system comprises of host rocks at and surrounding the repository.

![Figure 1.4. Sub-Surface Radioactive Waste Disposal modified after JAEA/FEPC (2007)](image)

Geological disposal of HLW in concrete constructs at least 300 m below the ground level.

Barrier materials are expected to exhibit abilities to retain and retard migration of radionuclides, including migration of any colloidal materials with radionuclides attached on them. The bentonite buffer and natural host rocks are porous media, and the interactions between radionuclides and barrier materials and their impacts on migration behaviors are of particular interest. Bentonite is composed mostly of montmorillonite, which is described chemically as a hydrous aluminum silicate, consisting of two tetrahedral sheets of Si-O separated by an octahedral sheet of Al-OH [10-11] (Figure 1.5). Bentonite is one of the key components of the engineered barrier system because of its swelling property, low permeability, and strong sorbing capacities for cations that are valuable for retardation of the migration of radionuclides [9, 12]. The host rock will form the last component of the multi-barrier system [12]. The properties of the host rocks will depend on the geology of the site selected for disposal facility,
however there are conditions favorable for the geological repository sites such as slow groundwater flow and reducing conditions that will limit the dissolution of radionuclides [12].

![Montmorillonite Crystal Structure](image)

**Figure 1.5. Montmorillonite Crystal Structure by Viani et al (2007) [11]**

### 1.1.3 High Level Waste (HLW) Repository Safety Assessment

Due to the high level of radioactivity as a result of high concentrations of long-lived radionuclides present in HLW, safety assessment must be carried out in order to evaluate the performance of the geological disposal system both during normal operation and after closing in order to meet the safety standards contained in the applicable regulatory stipulations [6,13-14]. Safety assessment is the process of using appropriate methods to analyze systematically the risks associated with the facility, and the ability of the site and the design of the facility to meet the minimum safety requirements and technical requirements [15]. For a quantitative assessment of the overall level of performance, it is necessary to acquire data through laboratory and field experiments to develop suitable mathematical models taking into account associated uncertainties and comparisons with design requirements and standards [15].

Among the tasks in safety assessment the determination of the relevant radionuclides and/or mechanisms of release and migration are included. The migration of radionuclides in the repository and in the subsurface environments has been considered to be controlled by their solubility and/or sorption to the buffer material and rock or soil matrix [16]. Radionuclides with low solubilities are not expected to dissolve in groundwater, thus will not be transported (immobile). In addition, radionuclides with high solubility become less mobile, or show
retarded migration when they strongly sorb onto the solid matrix. Examples of these radionuclides include Pu, Am, Eu, Cs and Sr.

However, these assumptions have been inconsistent with observations if radionuclides are attached to colloidal particles, since they were found to be mobilized. [16-17]. For example, it has been reported that Am released from a treated waste stream into a canyon at Los Alamos National Laboratory was detected more than 3 km away from the original source and was found to be strongly attached with colloids within the 25 to 430 nm size range [18]. Another study conducted in situ at the Grimsel Test Site (GTS) in Switzerland showed that when injecting radionuclides absorbed onto bentonite colloids in a fractured shear zone the majority of the Am and Pu migrated without retardation when associated with colloids [19]. The increasing evidence suggesting that colloids are enhancing the migration of radionuclides highlights the need to improve the current understanding of colloidal mediated transport of radionuclides, especially for the safety assessment of HLW repositories.

1.2 Colloid Interactions and Facilitated Transport

The migration of contaminants including radionuclides has been considered to occur in a two-phase system, the first phase is a mobile phase when contaminants are dissolved in a liquid or gas phase, and the second phase is an immobile phase when the contaminants are sorbed (attached or deposited) to the soil or rock matrix (Figure 1.6, left) [20-21]. However, recent field experiments and laboratory studies have shown that the transport of contaminant can be enhanced in the presence of mobile colloidal materials in aquifers [20] (Figure 1.6, right). Contaminants can sorb onto mobile colloids, they may migrate faster than the dissolved contaminants. This mechanism of contaminant migration is called colloid-facilitated transport.
1.2.1 Definition and Origin of Colloids

Colloids or nanoparticles are single molecule or polymolecule particles with at least one dimension having a size or diameter between 1 to 100 nm (sub-micron particles) that are dispersed in a medium [22]. Their small size allows them to remain suspended due to Brownian motion and are ultimately transported by groundwater if certain criteria are met. Particles with larger diameters of a few microns may settle due to gravitational forces [23], and smaller particles with diameters less than 1 nm are believed to behave as dissolved species [24]. Some recent studies have focused on small colloids with diameters less than 100 nm and clusters with diameters less than 10 nm and have shown that they exhibit properties that are not present in their bulk larger counterparts [25].

Naturally occurring colloids can be inorganic, primarily generated by mechanical fragmentation through erosion or weathering of the host rock in contact with groundwater caused either by chemical or physical perturbations such as changes in pH or flow rate [24] while organic colloids are typically humic materials (i.e., humic acid), formed by the breakdown of organic matter from recent biological origin or from much older origin such as from coal or lignite deposits [20]. Natural organic matter (NOM) that constitutes these organic colloids can be very complex macromolecules with a wide range of molecular weights and multiple functional groups. In addition, in the case of HLW repositories, colloids can also be generated from the degradation of the engineered barrier system materials including overpacks and bentonite backfill [26] and waste packages (i.e., iron or other metals) [27].
1.2.2 Colloidal Interactions with Surfaces

1.2.2.1 Derjaguin-Landau, Verwey and Overbeek (DLVO) Theory and Extended Derjaguin-Landau, Verwey and Overbeek (XDLVO) Theory

In order to understand and predict colloidal transport of contaminants in the environment, surface interactions of colloidal particles and their impact on migration behaviors have been widely studied. Interactions between charged colloidal particles, or colloidal particles and charged collector surfaces in solvent have been quantitatively described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [28-29]. The DLVO interactions consider two primary forces, van der Waals (vdW) and the electrostatic double layer (EDL) [28-29]. The origin of the vdW interactions is from the interplay of electron distributions and polarizability between molecules and the medium [30] and are usually attractive. The EDL is formed because the majority of surfaces will likely be electrically charged in water [31], and this electric field will attract counterions, and as a result a diffuse layer of counterions is formed on top of the surface charge layer [32].

The DLVO theory considers the total interaction energy \( U_{DLVO} \) as the sum of the attractive van der Waals forces \( U_{vdW} \) and the repulsive electrostatic double layer forces \( U_{EDL} \), and it can be either repulsive or attractive depending on factors such as the chemical structure, suspending medium, geometry and surface potential [33]. The total interaction energy \( U_{DLVO} \) is expressed as:

\[
U_{DLVO} = U_{vdW} + U_{EDL}
\]

The DLVO interaction energy is described usually as an interaction energy plot or curve where the total interaction energy of charged surfaces is plotted as a function of surface separation distance (Figure 1.7). Positive DLVO interaction energies indicate repulsive interactions producing stability of the colloidal particles (Figure 1.7, blue line) and negative values indicate attractive interactions that can result in attachment and/or aggregation (Figure 1.7, red line). Another possibility is that the repulsive interaction energy keeps increasing as the two surfaces approach closer until they overcome the energy barrier (primary energy barrier), at which point the interactions become less repulsive. At separation distances shorter than the primary energy...
barrier distance, they become attractive (Figure 1.7, green line). There is a possibility that another attractive region is formed at long separation distances from the primary energy barrier resulting from the attractive vdW interactions decaying slower than the EDL repulsions [34]. This region is called the secondary minimum (Figure 1.7, right side). The strength of the vdW forces is determined by the size and the shape of the colloids or nanoparticles and by the chemical nature of the system involved, usually described by the Hamaker constants [35].

![Figure 1.7. DLVO Total Interaction Energy Curve](image)

Recently, forces other than vdW and EDL have been considered to influence colloidal interactions. These non-DLVO forces have been used to model experimental results, and the models have been called the extended DLVO theory (XDLVO) [36]. The additional forces considered in the XDLVO can include steric repulsive [37], bridging [38], osmotic [37], hydrophobic Lewis acid-base [39] and magnetic forces [40]. The relevance of each force depends on the system tested, and often more than one XDLVO forces are significant when these forces are not completely independent from one another, making application of the XDLVO theory difficult [36]. Thus, it still is a great challenge to apply current models for
interactions and transport of colloidal particles especially in complicated systems such as in natural environments [33].

1.2.3 Mathematical Models for the Transport of Colloids

Mathematical models have been developed in an attempt to describe colloid transport and retention. Controlling processes of the transport of colloids or nanoparticles in the natural subsurface can include physical and chemical interactions at solid-aqueous interfaces as well as flow and transport. The most common model used is described briefly in the following sections.

1.2.3.1 One Dimensional Advection Dispersion (1D-AD)

Mass conservation of non-reactive solutes transported through a porous media is usually described with the one-dimensional advection-dispersion equation (1D-ADE) partial differential equation. It considers that the solute transport is through a thin column, which has the inner diameter significantly shorter than the column length, packed with a homogeneous porous media. The solution is injected from an inlet located at one end of the column. The 1D-AD model considers that the advective flux is described as Equation 1.2 and that the dispersive flux is driven by a concentration gradient, typically described by Fick’s law (Equation 1.3).

The advective flux ($J_{adv}$) can be expressed as:

$$J_{adv} = vC \quad (1.2)$$

where $v$ is the linear fluid velocity (m/s) and $C$ is the concentration (mol/m³).

The dispersive flux ($J_{disp}$) is usually described with the Fick’s law:

$$J_{disp} = -D \nabla C \quad (1.3)$$

where $D$ is the molecular diffusion coefficient (m²/s), $C$ is the concentration (mol/m³) and $\nabla$ represents gradient.
The total flux is given by the sum of both Equations 1.2 and 1.3 as follows:

\[ J_{\text{total}} = J_{\text{adv}} + J_{\text{disp}} = \nu C - D \nabla C \quad (1.4) \]

By combining advection and dispersion transport processes with the continuity equation (Equation 1.5), an expression for the mass conservation of a non-reactive solute is obtained as follows:

\[ \frac{\partial C}{\partial t} = -\nabla \cdot J_{\text{total}} \quad (1.5) \]

Substitution of Equation 1.4 into Equation 1.5 yields:

\[ \frac{\partial C}{\partial t} = -\nabla \cdot (\nu C - D \nabla C) \quad (1.6) \]

The 1D-ADE is Equation 1.6, and for one dimensional system it can be simplified as follows:

\[ \frac{\partial C}{\partial t} = -\nu \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \quad (1.7) \]

where \( C \) is solute concentration (mol/m\(^3\)), \( \nu \) is the flow velocity (m/s), \( D \) is the diffusion coefficient (m\(^2\)/s), while \( t \) and \( x \) represent time (s) and separation distance (m) respectively.

### 1.2.3.2 Colloid Filtration Theory (CFT)

The Colloid Filtration Theory (CFT) has been widely used to model transport of colloidal materials through porous media [41]. The CFT considers the deposition of colloids as a two-step process: the first step is the transport of colloid to the collector surface [42], and the second step is the attachment to the collector surface [42-43]. The transport to the collector surface is quantified by the frequency at which suspended particles contact the solid phase, and the parameter is called the single collector contact efficiency (\( \eta_0 \)) [43]. The suspended particles are considered to contact the surface of a collector due to three mechanisms: interception, gravitational sedimentation and Brownian diffusion [41, 44]. Brownian diffusion is especially
important for the retention of particles because a high diffusivity leads to an increase of collisions with the surface of the collectors [45]. The single-collector contact efficiency can be determined as Equation 1.8 by addition of the contributions of three contact mechanisms [46]:

\[
\eta_0 = \eta_D + \eta_I + \eta_G \quad (1.8)
\]

where \(\eta_D\) is transport by diffusion, \(\eta_I\) transport by interception and \(\eta_G\) is transport due to gravity and there are separate correlation equations to estimate contacts by each mechanism.

The single collector contact efficiency \((\eta_0)\) is considered to be a function of four dimensionless quantities as shown in Equation 1.9 [44, 46]:

\[
\eta_0 = \eta_0(N_R, N_{Pe}, N_{vdW}, N_{gr}) \quad (1.9)
\]

where \(N_R\) is the aspect ratio, \(N_{Pe}\) is the Peclet number, \(N_{vdW}\) is the van der Waals number and \(N_{gr}\) is the gravitational number defined in Table 1.2.

### Table 1.2 Dimensionless Parameters Governing Particle Filtration

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_R)</td>
<td>(d_p/d_c)</td>
</tr>
<tr>
<td>(N_{Pe})</td>
<td>(Ud_c/D_{\infty})</td>
</tr>
<tr>
<td>(N_{vdW})</td>
<td>(A/k_BT)</td>
</tr>
<tr>
<td>(N_{gr})</td>
<td>(4/3 [(\pi d_p^4(\rho_p-\rho_f)g)/k_BT])</td>
</tr>
<tr>
<td>(N_A)</td>
<td>(A/(12\pi\mu a_p^2U))</td>
</tr>
<tr>
<td>(N_G)</td>
<td>(2/9 (a_p^2(\rho_p-\rho_f)g)/\mu U)</td>
</tr>
<tr>
<td>(A_S)</td>
<td>(2(1-\gamma)/(2-3\gamma+3\gamma^2-2\gamma^3))</td>
</tr>
</tbody>
</table>

\(d_p\): particle diameter (m)  
\(d_c\): collector diameter (m)
$U$: fluid approach velocity (m/s)

$D_\infty$: bulk diffusion coefficient (described by Stokes-Einstein equation) (m$^2$/s)

$A$: Hamaker constant (J)

$k_B$: Boltzmann constant

$T$: absolute temperature (K)

$a$: particle radius (m)

$\rho_p$: particle density (kg/m$^3$)

$\rho_f$: fluid density (kg/m$^3$)

$\mu$: the absolute fluid viscosity (kg/m*s)

$\gamma = (1-f)^{1/3}$ where $f$ is the porosity of the porous medium

$g$: gravitational acceleration (m/s$^2$).

There is an empirical equation widely used to estimate $\eta_0$ in saturated porous media, which is shown in Equation 1.10 [47]. In this equation, collector particles are assumed to be spherical and their size as homogeneous [48]. It is considered to be suitable for application in natural environment because it accounts for hydrodynamic interactions and vdW attractive forces:

$$\eta_0 = 2.44 A_S^{1/3}N_R^{-0.081}N_{pe}^{-0.715}N_{vdW}^{0.052} + 0.55A_S N_R^{1.675}N_A^{0.125} + 0.22N_R^{-0.24}N_G^{1.11}N_{vdW}^{0.053}$$

(1.10)

The attachment to the collector surface is quantified by the frequency of collisions between suspended particles and the collector surface that result in attachment [47]. This parameter is called the empirical attachment efficiency ($\alpha$). The attachment efficiency ($\alpha$) is defined as the ratio of the single-collector removal efficiency ($\eta$) over the single-collector contact efficiency ($\eta_0$) as shown in Equation 1.11. The single-collector removal efficiency ($\eta$) is the number of particles that attach to the collector surface, and it is smaller than the number of collisions ($\eta_0$) when there is repulsion between the particle and the collector surfaces. The attachment efficiency represents the fraction of collisions between the suspended particles and the collector surface that results in particle attachment or deposition.

$$\eta = \alpha \eta_0$$

(1.11)
The attachment efficiency from column experiments is determined by the following equation [47]:

$$\alpha = \frac{2}{3} \frac{d_c}{(1-f)\mu L} \ln \left( \frac{C}{C_0} \right) \quad (1.12)$$

where $L$ is the packed medium length, and $C/C_0$ is the relative concentration obtained from the effluents under clean bed conditions at the initial stage of the breakthrough curve [47]. Equation 1.12 describes the ratio between the experimental $\eta$ and the predicted $\eta_0$ obtained from the empirical equation 1.10.

### 1.3 Gold Nanoparticles (AuNPs) Application as a Model Colloid to Understand Colloidal Interactions and Transport

#### 1.3.1 Migration Behavior of Natural Colloids

A portion of contaminants including radionuclides present in aquatic environments are often associated with particles and colloidal materials [19, 20]. Although significant progress has been made in understanding speciation of radionuclides [49] as well as their sorption behavior on surfaces [19, 20], migration behaviors especially of contaminants associated with colloids are an active area of research. Migration of large colloids ($\sim 10 \mu m$) is relatively simple since their retention is usually caused either by filtration by porous media or by gravitational settling [50]. However, migration of smaller colloids and/or nanoparticles is much more complicated because they can be transported through the pores with groundwater for long distances before they are absorbed onto the solid phase [45, 49] or before they form aggregates and sediment [50]. Presence of NOM can further complicate the migration of colloids because it can alter the colloidal stability and affect aggregation such as when NOM is adsorbed and covers the surface of colloids [45, 49].

The deposition and/or aggregation of colloidal particles in water-saturated porous medium are controlled by the nature of the colloid-collector and/or colloid–colloid interactions and they can alter the migration of colloidal particles in the environment [51]. Colloid-collector interactions can produce deposition of colloids onto the surface of the collector particles (porous media) and attractive colloid-colloid interactions can produce particle aggregation [51].
These colloidal interactions in aqueous solutions can be affected by certain physicochemical properties of both the colloids and collectors involved in a system, such as pH, ionic strength and surface charge since they can modify the EDL and/or vDW interactions (DLVO interactions) which are considered to govern particle aggregation and deposition [28-29].

A wide range of colloidal particles with a variety of physicochemical properties including sizes and compositions can exist in natural environments, making it difficult to characterize and directly study their behaviors [52]. To understand complex colloidal systems, the use of engineered nanoparticles with defined properties may be advantageous because they can be applied to investigate how colloidal interactions affect the transport mechanisms [53]. Understandings on how colloidal particles migrate in groundwaters may advance the reliability of the safety assessments regarding HLW repositories.

1.3.2 Synthesis, Assembly and Physicochemical Properties of AuNPs

Gold nanoparticles (AuNPs) possess unique physical and chemical properties that has made them useful in diverse areas including novel chemical and biological sensing [54]. The methods used to prepare AuNPs have expanded since their inception, and involve the treatment of chloroauric acid (HAuCl₄) with citric acid as a reducing agent (Figure 1.8) [55], and more recent methods include the direct reduction with sodium borohydride (NaBH₄) [56] or hydroquinone (C₆H₄(OH)₂) [57].

![Figure 1.8. Synthesis of AuNPs Using Sodium Citrate](image)

Synthesis method of AuNPs by the Turkevich method.
Nanoscale AuNPs can be prepared in a wide size range (Figure 1.9) and with many morphologies (i.e., spherical, cubical and nanorods) through the different synthetic methods developed [55-58], especially in the recent years, such as by changing the gold-to-reducing agent ratio, reaction speed and/or by two-step functionalization [54, 59].

![Figure 1.9 Size Hierarchy of Gold Compounds modified after Christian et al (2008)](image)

Figure 1.9. Size Hierarchy of Gold Compounds modified after Christian et al (2008) [62]
Gold compounds defined by size and number of atoms.

Furthermore, AuNPs properties can be customized and/or controlled since they can be prepared with different surface chemistry/coating that can alter their properties (Figure 1.10), therefore greatly increasing their potential applications [24].

![Figure 1.10 Schematic illustration of Surface Modified AuNPs](image)

Figure 1.10. Schematic illustration of Surface Modified AuNPs
Schematic of the shell and core structure of AuNPs.

The tunable properties of nanoparticles and especially AuNPs, can include properties such as higher stability, size-related electronic, magnetic and optical properties [28]. Bare (uncoated) and coated surface-modified metal nanoparticles can exhibit chromatic changes due to differences in their light scattering mechanisms. These chromatic changes arise from the
localized surface plasmon resonance (LSPR) effect resulting from the collective oscillation of the conduction electrons on the gold-core (Figure 1.11) due resonant excitation by incoming photons [54, 59-60].

![Figure 1.11. Localized Surface Plasmon Resonance (LSPR) Effect](image)

Schematic of localized surface plasmon resonance.

The LSPR effect in nanoparticles is unique because they have a much higher number of electrons per surface unit (i.e., electrons/nm²) compared to their bulk material counterparts [60], which for AuNPs the resonance properties are observable in the visible spectrum wavelengths therefore showing the unusual and intense colors. The LSPR is known to vary depending not only on a single property of the nanoparticles but is susceptible to other effects such as their chemical nature, nanoparticle size, shape and surface modification. The LSPR has been proven to be effective in detecting aggregation of AuNPs as absorption spectra changes when the interparticle distance changes [60]. Therefore, variations in the visible light absorption spectra of AuNPs can be used to monitor changes in intrinsic properties of the nanoparticle, which is the basis for many sensing and imaging applications [24].

1.3.3 Functionalization of AuNPs and Applications

Several reports exist on the application of both bare (uncoated) AuNPs and coated surface modified AuNPs. They are used as spectrophotometric agents due to their optical properties [54]. By controlling the size and surface functionalization of AuNPs, their interactions in solution with other nanoparticles, solvent, or other surfaces can be altered, making them attractive candidates for a great number of applications [54, 59].
Surfaces of AuNPs are usually coated with organic capping layers such as citrate [55] (Figure 1.8) and triphenylphosphine [61] (Figure 1.12) to improve the stability of the nanoparticles by increasing the electrostatic repulsions between nanoparticles so that aggregation is blocked. However, the stability can be susceptible to different solution characteristics such as pH, ionic strength, temperature or in non-aqueous solutions (i.e., organic solvents) [62].

![Triphenyl Phosphine Chemical Structure](image)

**Figure 1.12. Chemical Structure of Triphenyl Phosphine**

Triphenylphosphine chemical structure.

A common alternative to increase the stability of nanoparticles is to coat or shield the Au-core with long polymeric chains. This is usually achieved by attaching thiol-containing polymers as capping layers that counteract the attractive forces that might occur between nanoparticles (i.e., vdW forces), which can lead to aggregation [63-64].

### 1.3.3.1 PEGylated AuNPs

One of the common polymer coatings used to stabilize nanoparticles is poly (ethylene glycol) (PEG) (Figure 1.13) [65-68]. The process of covalent or non-covalent attachment of PEG ligands is called PEGylation. The solutions interpenetrate the polymer shell, and the PEG coatings hydrodynamically and sterically shield the AuNPs core, resulting in an increase in colloidal stability as a result of increased surfaces separation distances, thus preventing the attractive vdW forces [69].
The shielding abilities have been reported vary depending on the PEG conformations (Figure 1.14), the grafting density (Γ) in ligands/nm² [70-72], ligand molecular weight [73] and solvent nature [74]. If the Γ is sufficiently low (Figure 1.14A), the PEG chains prefer to adopt a “mushroom” configuration and if the Γ is high (Figure 1.14B) the ligands minimize their collective free energy by extending into a “brush” conformation [70].

Furthermore, the thickness of PEG ligand has been shown to be influenced by the surface curvature of AuNPs. Smaller nanoparticles usually show a higher density of ligands (i.e., PEG). The higher surface curvature probably causes a reduction in steric hindrance, since the free
ends of the PEG molecules are less confined [75-76]. Among the most commonly used PEG molecules is methyl thiol-containing poly (ethylene glycol) (PEG) (Figure 1.15). It has been used to cover several types of AuNPs by attaching the PEG chains to the Au-core by the strong sulfur-gold (S-Au) bonds, with the aims to introduce water solubility, surface charge screening, and increased colloidal stability [73, 76]. The properties of PEG coated AuNPs are very useful and they are exploited in many applications [54].

![Chemical Structure of Thiol-PEG](image)

**Figure 1.15. Chemical Structure of Thiol-PEG**

Chemical Structure of a thiol-PEG.

### 1.3.4 AuNPs for Environmental Applications

The migration behavior of functionalized AuNPs within complex environments has gained interest because the AuNPs possess physicochemical properties which are easy to characterize and detect [53], and because they can exist in the same size regime as natural colloidal materials (~1 - 200 nm) [53]. AuNPs can be used to study migration behaviors of colloids in relation to their physicochemical properties [53]. For example, retention studies of AuNPs in heterogeneous rock showed that colloid retention on granite was found to be strongly dependent on small scale chemical effects, roughness or non-uniform distribution of charged sites [77]. The experiments were conducted at two different pH to account for different rock–colloid electrostatic interactions: in the first case, the granite rock has positively charged minerals and the nanoparticles are negatively charged which results in favorable attraction, and in the second case, the granite minerals and the Au nanoparticles are both negatively charged, which results in unfavorable attraction. The micro-particle induced X-Ray emission (μPIXE) technique was used to visualize and quantify the colloid retention since AuNPs were highly stable and easily detected.

Another study compared the transport properties of two AuNPs with same core size but with two different surface coatings (citrate and bovine serum) at different ionic strengths (IS) by
observing the LSPR behavior [78]. Batch experiments showed that the stability against aggregation was higher for the AuNPs covered with bovine serum than with citrate at high ionic strengths (IS), attributed probably to the influence of their longer surface layer on the stability of the AuNPs which inhibited interactions with the porous media to occur. In column transport experiments, the bovine serum coated AuNPs were found to deposit and aggregate less than the citrate covered AuNPs, also likely to be caused by the stability provided by the bovine serum layer.

The AuNPs unusual and flexible physicochemical, optical and electrical properties as well as their high stability and variable size are beneficial characteristics for the understanding of colloidal interactions. The localized surface plasmon resonance properties of AuNPs allows easy detection and can also be used to monitor the local environment of the nanoparticles. The LSPR is dependent on the particle size, shape or interparticle distance, thus changes in the LSPR can indicate that alterations of the AuNPs properties occurred as a consequence of colloidal interactions. AuNPs have the potential to be employed in transport experiments in porous media in order to observe possible colorimetric changes due to alterations of their LSPR as a consequence of colloidal interactions with the porous media particles such as aggregation or other factors that can alter the migration behavior of colloidal particles. The understanding of colloidal interactions is a factor that needs to be taken into consideration for the safety assessment of geological repositories since colloidal material is ubiquitous to underground environments and their interaction with radionuclides will likely occur and if associated can become mobile.

1.4 Research Objective and Thesis Outline

For the safe design of HLW repositories that will isolate for long-term the waste generated from nuclear generation of energy, studies on the natural and engineered barrier functions under current and future conditions, as well as during unexpected disturbances, must be performed. In this sense, the understanding of colloidal mediated transport of radionuclides is highly important, since it can enhance their mobility in situations even when their mobility is not expected. Investigation of the factors that have impact on the transport and mobility of colloidal material in the geofluids is key in order to be able to predict and to model the migration behavior of radionuclides.
The use of model colloids/nanoparticles can be useful in elucidating the main transport and deposition mechanisms and the parameters that control it. The ability to use nanoparticles with customizable and unique properties such as AuNPs allows for their easy characterization and for the understanding of interactions with other nanoparticles as well as with the surrounding environment by correlating properties to effects. In this work, different-sized AuNPs were employed in either transport and/or batch experiments as model colloids in order to investigate the properties or mechanisms that can modify their interactions with barrier materials (natural or engineered) to understand their role in their migration behavior, which can also be applicable for naturally occurring colloidal materials and/or nanoparticles.

This thesis is composed of the following five sections, which are briefly discussed in the following paragraphs.

In **Chapter 1**, the generation of radioactive waste from the generation of power and other applications is presented, and the Japanese radioactive waste management program and waste classification is presented, including the concepts for intermediate-depth and deep geological disposal of radioactive waste. The multibarrier or engineered system is presented and described, where the performance or safety assessment of HLW repositories needs to include all the possible ways which radionuclides can migrate in the environment, including one of the most recently considered mechanism, colloidal mediated transport. The relevance and importance of colloidal facilitated transport is highlighted and the challenges of its further investigations. In this regard, colloids are defined, and their origins are presented as well as their potential interactions and the currently available mathematical models. Furthermore, the potential application of AuNPs as model colloids is proposed due to their surface functionalization abilities, useful in order to obtain a more complete understanding of the potential relationships between the properties of the nanoparticles with their interactions with the geomedia and effects in transport.

In **Chapter 2**, batch and transport experiments using three different sizes of AuNPs were carried out in a porous media composed of silica sand. The model AuNPs were characterized by size (in solution and dry), surface charge, surface coating length and optical properties (absorption spectra). The silica sand porous media was also characterized in size, morphology and in chemical composition. Transport breakthrough curves (BTCs) were obtained for the AuNPs and compared with the tritiated water (HTO), the HTO profile was modeled based on
the advection-dispersion equation however the AuNPs showed differences in their transport behavior. The transport differences are discussed, and possible explanations are proposed. Batch experiments were carried out to understand the AuNPs colloidal stability and interactions with silica sand. The absorbance spectra of each AuNPs were used to monitor changes in the concentration and in the properties of the AuNPs including aggregation. The transport and deposition of the AuNPs was evaluated using the DLVO theory and the most recent equations for calculating the attachment efficiency in order to understand and explain the experimental results.

In Chapter 3, different sized PEG-coated AuNPs deposition and/or aggregation behavior in systems with silica sand grains were studied by electron microscope and surface chemical analyses to elucidate their correlation with the AuNPs batch and transport behavior. Batch experiments with the different AuNPs onto silica sand grains were carried out, where random samples were extracted, vacuum dried and prepared for scanning electron microscopy imaging. The surfaces of the silica sand grains were studied and analyzed, several images were obtained from different grains at different magnifications and elemental compositions analyses were also performed to confirm the local chemical composition of the geomedia and to confirm the presence of AuNPs. The attachment behavior of the AuNPs observed in the SEM images showed consistency with the results from the deposition and transport experiments where the UV-Vis absorption spectra suggested that aggregation occurred and that it was likely the reason of increased column retentions for the larger AuNPs but less for the smaller ones. The deposition behavior onto the silica sand due to interactions with the sand surfaces likely occurred and their impacts on their transport behavior are discussed and correlations with local physical and chemical heterogeneities found on the silica sand surfaces are discussed.

In Chapter 4, the interactions between different sized PEGylated AuNPs with clay material (sodium montmorillonite) considered to be used as HLW buffer material were studied. Batch experiments at low pH values were performed to test the attachment between clay particles and AuNPs due to the formation of oppositely charged sites on the clay surfaces. The dispersion and attachment and/or deposition of different AuNPs with Na-montmorillonite particles were studied by UV-Vis, electron microscopy and energy dispersive X-ray spectroscopy. The possible parameters that control the nature of the interactions that take part into the attachment behavior between the AuNPs and the clay are proposed and correlated to the properties of the interacting materials. The interactions and attachment of the AuNPs were evaluated using the
DLVO theory including possible attachment modes between the particles considering both surface or edge interactions in order to understand and explain the experimental results. The experimental results using clay and the observed interaction differences are presented and discussed. The interactions between AuNPs and clay particles and with silica sand are compared and the differences are discussed.

In **Chapter 5**, the main conclusions and most relevant findings of this thesis are presented and summarized as a series of brief statements.
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Chapter 2. Transport of Gold Nanoparticles in Saturated Silica Sand Packed Columns
2.1 Introduction

High-level radioactive waste (HLW) has been planned to be disposed of in deep geological repositories. The repositories will consist of a multi-barrier system of engineered and natural barriers, which are expected to retard the migration of radionuclides to the biosphere for long periods of time [1, 2]. Thus, it is important to study migration behaviors of radionuclides through engineered and natural barriers for the safety assessment of deep geological disposal repositories [3].

One of the processes that can affect migration behaviors of radionuclides in natural and engineered barriers is colloid facilitated transport. In groundwater systems in and near deep geological repositories, a variety of types of colloidal particles exist with wide size distributions (from ~1 nm to ~1 μm). Colloids can be inorganic, such as common mineral particles (e.g., clay, metal oxides), organic (e.g., humic substances), and microorganisms such as viruses and bacteria [4-10]. In addition, colloidal materials can be produced from the components in the repositories, such as steel canisters, waste glass, bentonite, and concrete through processes such as degradation and/or erosion [11, 12]. These colloids can mobilize sorbed radionuclides in groundwater [13]. Experiments performed at the Grimsel Test Site in Switzerland found that radionuclides associated with bentonite colloids migrated without retardation [14]. Field investigations at the Los Alamos site showed that radionuclides associated with colloids were detected over 3 km from the source [15].

Fate and transport of colloids can be significantly affected by deposition and/or aggregation resulting from interactions between colloids and porous media, or between colloids themselves. Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory is the most commonly used model to predict colloidal interactions considering electrostatic double layer (EDL) and van der Waals (vdW) forces. However, discrepancies between DLVO predictions and experimental results have been observed and they have been attributed to non-DLVO forces, such as short-ranged Lewis acid-base interactions, bridging, steric, and magnetic forces [16-19]. Extended DLVO (XDLVO) theory including these forces have been proposed, however it has been challenging to understand the mechanism of colloidal behavior and to identify the relevant forces in any one system because colloidal interactions are complex with multiple and often interdependent forces [20].
In order to further understand the transport mechanisms of colloids in relation to their physical and chemical properties, the use of engineered nanoparticles as surrogates of colloidal materials has a potential. Some engineered nanoparticles have tunable sizes and surface functionalization abilities with specific optical and electronic properties [21-24], resulting in a great number of applications in the field including biology, catalysis, and optoelectronics [25-33]. In these applications, nanoparticles are usually stabilized by coating with organic capping layers (e.g., citrate [34], triphenylphosphine [35]), and they functionalize the surfaces as well as increase the electrostatic repulsions between nanoparticles to block aggregation.

Some bare and surface modified nanoparticles possess spectrophotometric properties [25-27], which can indicate changes in their properties such as nanoparticle size, surface modification and aggregation state. Citrate capped (uncoated) gold nanoparticles (AuNPs) have been used to study migration behaviors of colloids in natural soil matrices, and it has been reported that electrostatic interactions between the AuNPs and the ge media and formation of AuNP aggregates affect the mobility of the AuNPs [36-38]. However, these phenomena have not been fully understood, since interactions between the AuNPs and ge media are susceptible to both the properties of colloids and the surrounding conditions such as solution pH, ionic strength (IS), temperature and surface chemistry [38].

In this study, PEG-modified AuNPs of three different sizes were used as surrogates of colloids in batch deposition and column transport experiments in order to elucidate colloids transport behaviors in ge media in relation to colloidal properties. Au-cores used in this study were coated with thiolated poly (ethylene glycol) (PEG) as stabilizing ligands, and the coating of the AuNPs with three different sizes have the same molecular weight. PEG is widely used since it provides great water solubility and colloidal stability through steric effects [39-42], which can counteract the attractive forces that might occur between nanoparticles without disturbing other interactions such as the charge of the core [43-45].

Silica sand was used as ge media because of the simplicity of the chemical composition and pore structure in the column. The focus of the study is to compare the mobility of AuNPs through silica sand in relation to physical and chemical properties of AuNPs and silica sand. The stability of the AuNPs under different IS conditions was studied in batch experiments. The AuNPs properties were characterized and their influence on the transport behavior and stability were investigated.
The purpose of this study is to further understand the mechanisms of nano-sized colloid transport, which is necessary to evaluate the impact of colloidal transport on safety assessment in geological disposal.

2.2 Materials and Methods

2.2.1 Gold Nanoparticles (AuNPs) and Porous Media

AuNPs of three different nominal diameters (10 nm; AuNP10, 50 nm; AuNP50, and 100 nm; AuNP100, NanoXact, Nanocomposix, USA) were used in this study, and they were coated with poly (ethylene glycol)-methyl ether thiol of ~ 5 kDa. The Au concentrations in the stock solutions of AuNP10, AuNP50 and AuNP100 were 52, 54 and 52 mg/L, respectively. These stock solutions were kept and stored in the dark at 5 °C and used by diluting with deionized (DI) water after it was vortexed or sonicated. The silica sand sample used as porous media in this study was Albany silica sand grains (99.8% SiO$_2$, Tochu, Japan) of high purity with an average particle size of 0.425 mm.

2.2.2 Characterization Methods of the AuNPs and Porous Media

The AuNPs ultraviolet-visible (UV-Vis) absorption spectra were obtained to confirm the AuNPs localized surface plasmon resonance (LSPR) bands and to quantify the AuNPs concentrations (Hitachi U-5100; Shimadzu UV-1800, Japan). Multiple calibration curves were obtained to determine AuNPs concentration based on the maximum absorbance of the solutions at their LSPR wavelength, all with consistent correlation.

Transmission Electron Microscopy (TEM) images were obtained to determine the AuNPs gold-core diameter ($d_{TEM}$) and morphology (JEOL JEM-2010, Japan) with an electron microscope operating at 200 kV. The TEM samples were prepared by air drying a small droplet of the individual AuNPs suspensions over a carbon/Cu grid (200 mesh, JEOL, Japan) overnight.

The average size of each AuNPs was determined by the analysis of images captured at high magnification with at least 3 particles per image, in at least three randomly selected regions.
The hydrodynamic diameters ($d_{DLS}$) and zeta potential ($\zeta$-potential) of the AuNPs were measured in DI water using Dynamic Light Scattering (DLS) and electrophoretic light scattering (ELS) analyses (Delsa Nano HC, Beckman Coulter, USA) respectively.

Scanning electron microscopy (SEM) image analysis (JEOL, JSM-7001FA, Japan) was conducted for the silica sand sample to observe average diameter and surface morphology. Energy dispersive X-ray spectroscopy (EDS) was carried to determine the elemental composition of the sand particles.

2.2.3 Batch Deposition Experiments

Batch experiments were conducted to examine the AuNPs colloidal stability and deposition behavior in the presence of silica sand particles. Concisely, 0.10 g of silica sand were introduced into a series of 15 mL Corning centrifuge tubes and mixed with 10 mL of AuNPs solution. The AuNPs concentrations of AuNP10, AuNP50, and AuNP100 solutions were $\sim$ 13, $\sim$ 13.5, and $\sim$ 13 mg/L, respectively. The suspensions of AuNPs and sand were gently mixed with an oscillating tube shaker working at $\sim$ 80 min$^{-1}$ (Water bath/Shaker, Taitec Co., Japan) for 1 h. Ambient light was shielded during experiments. The supernatant fluids were decanted and filtered with a 0.45 $\mu$m syringe filter and their concentrations were measured by UV-Vis spectrophotometry. Control experiments under the same conditions without silica sand were performed. The aliquots taken from the control experiments were also analyzed by UV-Vis periodically.

2.2.4 AuNPs Colloidal Stability Experiments

The stability of the AuNPs attached with PEG was investigated by time-resolved UV-Vis spectroscopy. 0.5 mL of AuNPs solutions with concentrations $\sim$ 13 mg/L for AuNP10, $\sim$ 13.5 mg/L for AuNP50, and $\sim$ 13 mg/L for AuNP100 were added to tubes and the IS was adjusted to values between 10 mM to 29 mM by adding NaCl (Junsei Chemical, 99.5%) stock salt solution. Immediately after the addition of the NaCl solution, the tubes were vortexed briefly to obtain a homogeneous mixture. The samples were also analyzed by UV-Vis spectroscopy after they were allowed to incubate for at least 10 min.
2.2.5 Column Transport Experiments

Transport experiments were performed using glass columns (EYELA, Japan) with dimensions of 2.0 cm (inner diameter) × 10 cm (length), filled with water-saturated silica sand (average size of 0.425 mm) as shown in Figure 2.1. The columns were dry packed with silica sand to the depth of 10 cm with a porosity (ε) of 0.41. The porosity (ε) of the column was determined from the difference between the dry and the water-saturated weights of a silica-sand packed column. Total pore volume (V_{pore}) was calculated by multiplying total porosity by the total volume of the columns. The columns ends were fitted with two 10 µm pore sized glass filters with Teflon packing (EYELA, Japan).

Previous to and during the injection, the AuNPs suspensions were under continuous stirring by using a magnetic stirring plate working at ~ 250 rpm and all the experiments were conducted covered from ambient light to eliminate any undesired effects. DI water was introduced into the column in an upwards flow manner for several hours at a flow rate of 1.5 mL/min, to fully saturate the column with water and to equilibrate the surface of the porous media before the start of any transport experiments.

![Figure 2.1. Transport Experiments Illustration](image)

Schematic of the experimental setup.

After complete saturation and conditioning of the column with DI water, 10 min pulse injections of suspensions of AuNP10, AuNP50, or AuNP100 (~ 13, ~ 13.5 or ~ 13 mg/L respectively) followed by DI water were introduced into the columns at a flow rate of 1.5 mL/min until no AuNPs were detected in the effluents. The DI water and the freshly prepared
AuNPs solutions were delivered by a HPLC pump (Shimadzu, LC-20AD, Japan) to ensure accurate and smooth flow during the experiments and the effluent fractions were collected at constant intervals using a fraction collector (Advantec, CHF1215A, Japan). The AuNPs column effluents were analyzed by UV-Vis spectrometry at their maximum absorbance peaks. The recovery of AuNPs was determined by numerically integrating the amount of AuNPs in the effluent from the breakthrough curves (BTCs). Representative recoveries were also calculated from the BTCs obtained using ICP-AES (Shimadzu, ICPS-9000, Japan) analysis of the effluents for AuNP10 and AuNP100.

Before and after an AuNPs transport experiment, tritium (HTO) solution of 80 Bq/mL (Perkin Elmer, USA) was injected as a nonreactive tracer in a way similar to the case of the DI water and AuNPs, in order to evaluate water flow and the hydrodynamic properties. The HTO effluents were collected using a fraction collector and the HTO concentrations were measured by a liquid scintillation counter (ALOKA, LSC-6100, Japan). All column experiments were run at room temperature and conducted at least in duplicate with good reproducibility.

2.3 Results

2.3.1 Properties and Characterizations of AuNPs and Silica Sand

Figure 2.2 shows the TEM images of AuNP10, AuNP50, and AuNP100. The nanoparticles were monodispersed and spherically shaped, with average Au-core diameters ($d_{TEM}$) of 10 ± 1, 51 ± 6 and 101 ± 16 nm for AuNP10, AuNP50 and AuNP100, respectively (Table 2.1).
Figure 2.3 shows the results of the DLS measurements for the AuNPs in DI water. The average hydrodynamic diameters ($d_{DLS}$) for the three nanoparticles were 43 ± 3 (AuNP10), 82 ± 1 (AuNP50) and 127 ± 3 nm (AuNP100) (Table 2.1), and the observed difference in particle size is attributed to the presence of the PEG layer since it cannot be detected by TEM measurements.

The thickness of the PEG polymeric coating was estimated by dividing the difference between $d_{TEM}$ and $d_{DLS}$ by a factor of 2. Although the same molecular weight PEG (~ 5 kDa) is used for all AuNPs, the thickness of the PEG layer decreased as the Au-core size increased.

The ζ-potentials of the AuNPs were found to be negative with values of -12 ± 0, -31 ± 1, and -25 ± 4 mV for AuNP10, AuNP50, and AuNP100 respectively (Table 2.1) in the DI water conditions used in the experiments (i.e., ~ pH 6).

Table 2.1 Physicochemical Properties of the AuNPs

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>$d_{TEM}$ (nm)</th>
<th>$d_{DLS}$ (nm)</th>
<th>PEG-layer thickness (nm)$^{1}$</th>
<th>ζ-potential (mV)</th>
<th>$\lambda_{max}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuNP10</td>
<td>10 ± 1</td>
<td>43 ± 3</td>
<td>17 ± 2</td>
<td>-12 ± 0</td>
<td>520</td>
</tr>
<tr>
<td>AuNP50</td>
<td>51 ± 6</td>
<td>82 ± 1</td>
<td>16 ± 3</td>
<td>-31 ± 1</td>
<td>530</td>
</tr>
<tr>
<td>AuNP100</td>
<td>101 ± 16</td>
<td>127 ± 3</td>
<td>13 ± 8</td>
<td>-25 ± 4</td>
<td>565</td>
</tr>
</tbody>
</table>

$^{1}$ PEG-layer calculated as ($d_{DLS} - d_{TEM}$)/2.

PEG coated AuNPs are less negative compared to the ζ-potentials for “bare” or uncoated gold nanoparticles of comparable sizes, which are around -40 mV [46]. The ζ-potentials were
measured at the surface plane of the PEG-layer ($d_{DLS}$); thus, these values reflect the shifts produced by the PEG-layer. They are neutral capping ligands and shield the negative charge that bare gold nanoparticle possesses. These results were in agreement with a previous study that showed the absolute $\zeta$-potentials of gold nanoparticles were reduced significantly with increasing thickness of the attached PEG units [47]. The sand grains are also negatively charged since typical values for the Point of Zero Charge (PZC) of silica sand have been reported to be at pH around 3.5 [48].

The AuNPs stock solution can be identified by their intense red colors. The UV-Vis spectra for the AuNPs are shown in Figure 2.4. The peaks corresponding to the localized surface plasmon resonance (LSPR) bands of the AuNPs are identified in Figure 2.4.

Figure 2.4. AuNPs UV-Vis Spectra

Normalized UV-Vis (in water) for (left) AuNP10, (middle) AuNP50 and (right) AuNP100.

Figure 2.5 shows the plots of the height of the maximum absorption peak as a function of the AuNP concentration. Good linear regression of the plots indicated that the concentration of the AuNPs can be evaluated from these UV-Vis calibration curves in the ranges of concentrations used in this study.
Figure 2.5. AuNPs UV-Vis Calibration Curves

UV-Vis absorption (maximum) for solutions of (left) AuNP10, (middle) AuNP50 and (right) AuNP100 plotted against AuNPs concentration.

Figure 2.6 shows representative SEM images of the silica sand particles. They were found to be mostly rounded prolate grains with discernible irregularities such as cavities and fractures on the surfaces.

Figure 2.6. Silica Sand SEM Images

SEM images for the silica sand particles at magnifications of (left) 95x and (right) 500x.

Trace amounts of impurities on the surface of the silica sand were identified by EDS elemental analysis, as shown in Figure 2.7.
Figure 2.7. Silica Sand SEM-EDS Spectra

SEM-EDS results for the composition of silica sand grains.

The results from the size and elemental analysis were in good agreement with the data provided by the manufacturer (Tochu, Japan) shown in Table 2.2.

Table 2.2 Silica Sand Chemical Composition*

<table>
<thead>
<tr>
<th>Composition</th>
<th>Silica Sand (Mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>99.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*Data provided by Tochu, Japan.

2.3.2 Stability and Aggregation of AuNPs in Batch Experiments

Samples of the AuNP solutions were kept in the dark for two weeks at room temperature, or several months refrigerated and no significant changes in UV-Vis spectra were observed.
including LSPR absorbance peak shifting, peak decline, peak broadening, or formation of secondary bands. This indicates long term stability of the AuNPs in aqueous solutions. The ionic strength of the AuNPs solutions were increased by adding NaCl to make various concentrations between 10 and 29 mM, in order to induce the aggregation of AuNPs. Higher IS compresses the EDL of the AuNPs, and as the EDL repulsive energy barriers are lowered, attractive forces including vdW interactions become more significant, resulting in AuNPs destabilization and aggregation.

**Figure 2.8** shows the UV-Vis spectra of the supernatant solutions obtained from the aggregation experiments. AuNP50 and AuNP100 showed a decline and a band broadening of the LSPR absorbance peak, and these effects became more evident as the NaCl concentrations increased. The degree of peak decline and band broadening indicates the significance of destabilization and aggregation caused by increasing IS. The UV-Vis spectra for AuNP10 did not show notable alterations until at the highest IS, suggesting that they were most resistant to destabilization and aggregation.

![Figure 2.8. AuNPs Batch Aggregation Experiments UV-Vis](image)

**Figure 2.8. AuNPs Batch Aggregation Experiments UV-Vis**
Normalized UV-Vis spectra (in water) of (a) AuNP10, (b) AuNP50 and (c) AuNP100 and at increasing concentrations of NaCl. The arrows indicate NaCl concentration increasing from 0 to 29 mM. Arrows indicate alteration on the UV-Vis spectra.

Batch deposition experiments with silica sand showed ~ 3 % deposition for AuNP50 and ~ 15 % for AuNP100, whereas the deposition of AuNP10 was minimal of ~ 1%. **Figure 2.9** shows the UV-Vis spectra of the supernatant before and after batch deposition experiments at the concentrations of ~12.87, ~13.01 and ~11.05 mg/L for AuNP10, AuNP50 and AuNP100.
respectively. The main absorption peaks were found to decline and broaden for AuNP50 and AuNP100, and it was most evident for AuNP100 (Figure 2.9, c).

Figure 2.9. AuNPs Batch Deposition Experiments UV-Vis
Normalized UV-Vis spectra (in water) of AuNP10 (a), AuNP50 (b) and AuNP100 (c) before and after the deposition experiments with silica sand. The arrows indicate UV-Vis spectral changes before and after mixing with sand.

The changes in the UV-Vis spectra were similar to the results from the aggregation experiments (Figure 2.8), indicating the presence of aggregated AuNPs in the supernatant solution. These results suggest that the interactions between silica sand and the AuNPs caused deposition and aggregation for AuNP50 and AuNP100, but minimal deposition/aggregation for AuNP10.

2.3.3 Column Transport of AuNPs

Figure 2.10 shows the representative BTCs from the transport experiments conducted with solutions of AuNP10, AuNP50, and AuNP100 through columns packed with silica sand. The normalized particle concentration ($C/C_0$) at the column effluent was plotted as a function of time.
Figure 2.10. AuNPs Breakthrough Curves (BTCs)

Breakthrough curves (BTCs) from saturated columns packed with silica sand for pulse injections of solutions of AuNP10, AuNP50 and AuNP100 at a flow rate of $Q = 1.5\text{mL/min}$. The breakthrough behavior for the nonreactive HTO tracer is also shown (dotted black line).

The BTC of HTO (Figure 2.10, dotted line) showed that it behaved as a non-reactive tracer and was in good agreement with the advection-dispersion equation. The BTC of HTO was symmetrical with a high recovery ($> 98\%$) of the HTO introduced into the column. The BTCs of HTO obtained before and after an AuNPs column transport experiment showed no significant changes (Figure 2.11), suggesting experiments with AuNPs did not almost change the pore structure.
The BTCs for the AuNP solutions were different from that of HTO (Figure 2.10). The initial breakthrough occurred almost at the same time as HTO, however, effluent AuNP concentrations did not increase as HTO (Figure 2.10, between ~ 7 to ~ 11 minutes). The differences between the BTC of AuNP and HTO were more significant for AuNP50 and AuNP100. In addition, the BTCs of AuNPs did not reach flat plateaus, but showed a sloping behavior (Figure 2.10, between ~ 12 to ~ 17 minutes). The maximum $C/C_0$ values in the plateau region did not reach one as HTO, but were ~ 0.96 for AuNP10, ~ 0.89 for AuNP50, and ~ 0.87 for AuNP100. After the influent solution was switched back to DI water, the AuNPs concentrations decreased to zero with a little tailing (Figure 2.10, between ~ 18 to ~ 30 minutes).

Figure 2.12 shows the evaluation of the UV-Vis spectra of the AuNPs column effluents. Alterations of the main absorption bands were observed for AuNP50 and AuNP100, such as decline, broadening and shifting between 530 - 532 nm and between 563 - 565 nm for AuNP50 and AuNP100, respectively (Figure 2.12, b and 2.12, c). These were similar to the spectra changes in batch stability and deposition experiments and may suggest aggregation. However, no notable changes in UV-Vis spectra were observed for AuNP10 (Figure 2.12, a), similar to the batch stability and deposition experiments.
Figure 2.12. AuNPs Breakthrough Curves (BTCs) Effluent UV-Vis Variation with Time
Normalized UV-Vis spectra (in water) of the column effluents of (a) AuNP10, (b) AuNP50 and (c) AuNP100 at different times. The arrows indicate time variation. Arrows indicate alteration on the UV-Vis spectra.

The recovery of AuNP10 in the column effluent was over ~ 95 %, whereas they were 88% and 85% for AuNP50 and AuNP100, respectively. Due to the changes in UV-Vis spectra of the column effluent possibly due to aggregation, the recoveries obtained from ICP-AES were compared to UV-Vis results, but the differences were negligibly small (~ 100 and 83% for AuNP10 and AuNP100 respectively).

2.4 Discussion

2.4.1 Interactions Between AuNPs and Silica Sand and Between AuNPs

Interactions between AuNPs and geological media can influence deposition, and between other AuNPs affect aggregation. Nanoparticle deposition and aggregation greatly affect the fate and transport in the geological environment. The batch deposition experiments showed significant deposition and aggregation of AuNP50 and AuNP100, whereas minimal deposition and aggregation was observed for AuNP10 (Figure 2.9). Batch stability experiments with increasing IS also showed aggregation of AuNP50 and AuNP100, but minimal for AuNP10 (Figure 2.8). AuNP10 exhibited increased stability against interactions with other surfaces such as silica sand and other AuNP particles, whereas AuNP50 and AuNP100 can be destabilized to form deposition and/or aggregation.
The estimation of the classical DLVO interaction energy was used to assist in the understanding of the mechanisms that can control the AuNPs deposition and aggregation observed in the experimental results. The DLVO theory states that the total interaction energy \( U^{DLVO} \) is the sum of the van der Waals (vdW) attractions \( U^{vdW} \) and the electrical double layer interaction energies \( U^{EDL} \) [49-50], and can be expressed by the following equation:

\[
U^{DLVO} = U^{vdW} + U^{EDL} \quad (2.2)
\]

where \( U^{DLVO} \) is the total interaction energy between the PEG layers of the AuNPs and the sand surfaces in water as a media (DI water was assumed with a low ionic strength 0.001 M). The considered interactions occurring between a single AuNP and a grain of silica sand in the column where taken as interactions between a perfect sphere and an infinitely long plate respectively, reasonable due to their relative size differences, and were calculated using the following equation [51]:

\[
U^{vdW} = -\left(\frac{A_{p}}{6h}\right)\left(1 + \frac{14h}{\lambda}\right)^{-1} \quad (2.3)
\]

where \( A \) is the Hamaker constant for the interacting surfaces (PEG and sand interacting in water); \( A_{p} \) is the AuNPs radius \( (d_{DLS}) \), \( h \) is the separating distance, and \( \lambda \) is a characteristic wavelength of the dielectric, usually considered to be 100 nm. The Hamaker constant between two materials and a medium \( A_{PEG/H2O/Si} \) was calculated using the Hamaker constants for vdW interactions of the materials in vacuum \( (A_{PEG}, A_{H2O} \text{ and } A_{Si}) \) in a third media [3] and were calculated with Equation (13). Considering previously reported values of Hamaker constants in vacuo for \( A_{H2O}, A_{PEG} \text{ and } A_{Si} \) \([52-53]\), the Hamaker constant for the system \( A_{PEG/H2O/Si} \) was calculated and found to be \( 5.94 \times 10^{-21} J \).

The \( U^{EDL} \) calculations were done with the following equation which has been developed for estimating interactions between a spherical particle and an infinitely flat plane assuming constant potential [54]:

\[
U^{EDL} = \pi \varepsilon_{0} \varepsilon_{r} A_{p} \left[ 2\zeta_{PEG}\zeta_{Sand} \ln \left( \frac{1+e^{-kh}}{1-e^{-kh}} \right) + \left( \zeta_{PEG}^2 + \zeta_{Sand}^2 \right) \ln \left( 1 - e^{-2kh} \right) \right] \quad (2.4)
\]
where $U^{EDL}$ is the electrostatic interaction energy between the PEG surface of the AuNPs and sand surfaces dispersed in a water medium, $\varepsilon_r$ is the relative permittivity of water (78.5), $\varepsilon_0$ is the permittivity of a vacuum ($8.854 \times 10^{-12}$), $a_p$ are the AuNPs radius ($d_{DLS}$ values were used), $\zeta_{PEG}$ are the surface potentials of the interacting surfaces (measured zeta potentials were used), the $\zeta_{Sand}$ used was $-32 \pm 0$ obtained following a similar method as [55], $h$ is the separation distance and $\kappa$ is the inverse Debye screening length, defined as:

$$k = \sqrt{\frac{e^2 \sum n_i z_i^2}{\varepsilon_0 \varepsilon_r k_B T}}$$ (2.5)

where $e$ is the electron charge ($1.60 \times 10^{-19}$ C), $n_i$ and $z_i$ are the number concentration and valence of ion $i$.

The DLVO interaction energies were also estimated to evaluate the aggregation behavior of AuNPs with the following equations for the $U^{vdW}$ and $U^{EDL}$ interactions between two spherical AuNP of similar size and were calculated as follows:

$$U^{vdW} = -\left(\frac{A}{6}\right) \left\{ \left( \frac{2a_p^2}{h(4a_p+h)} \right) + \left( \frac{2a_p^2}{2(a_p+h)^2} \right) + \ln \left( \frac{h(4a_p+h)}{(2a_p+h)^2} \right) \right\}$$ (2.6)

For the $U^{EDL}$ electrostatic interaction between two AuNPs, a simplified equation was used:

$$U^{EDL} = 2\pi \varepsilon_0 \varepsilon_r a_p \zeta_{PEG}^2 \ln(1 + e^{-kh})$$ (2.7)

The DLVO energy profiles for deposition on silica sand and aggregation are shown in Figures 2.13, 2.14 and 2.15 for AuNP10, AuNP50 and AuNP100 respectively after normalization by $k_B T$. 

Figure 2.13. DLVO Plot Describing Interactions of AuNP10-Sand and AuNP10-AuNP10

DLVO energy plot for interactions between AuNP10-AuNP10 (dashed line) and AuNP10-sand (solid line).

Figure 2.14. DLVO Plot Describing Interactions of AuNP50-Sand and AuNP50-AuNP50

DLVO energy plot for interactions between AuNP50-AuNP50 (dashed line) and AuNP50-sand (solid line).
Figure 2.15. DLVO Plot Describing Interactions of AuNP100-Sand and AuNP100-AuNP100

DLVO energy plot for interactions between AuNP100-AuNP100 (dashed line) and AuNP100-sand (solid line).

The obtained DLVO energy profiles (Figures 2.13 to 2.15) all show deep primary energy wells at smaller distances $h$ (irreversible interaction) followed by the maximum energy barriers (values shown in Table 2.3), where very shallow secondary minimum (less than 1 $k_B T$) appear several nanometers away from the surface. The classical DLVO theoretical calculations estimate that colloidal interactions occur only via vdW and EDL interactions thus it does not consider other possible interactions such as steric effects (i.e., entropic and osmotic contributions), therefore, it cannot represent all the possible interactions involving the PEG-coated AuNPs. However, qualitative explications regarding the role of the PEG-layers on the deposition and aggregation of the interacting surfaces can be obtained from the DLVO calculation results obtained.

When observing the calculated primary energy barriers for the different AuNPs, it can easily be observed that the energy barriers were much lower for aggregation than those for deposition onto silica sand (Table 2.3).
Table 2.3. Calculated Maximum Energy Barriers \( (U_{DLVO}) \) and Distances for AuNPs Interacting with Sand and With Another AuNPs.

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Deposition Energy Barrier</th>
<th>Aggregation Energy Barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( U_{DLVO} ) ( (k_B T) )</td>
<td>Distance ( h ) ( (nm) )</td>
</tr>
<tr>
<td>AuNP10</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>AuNP50</td>
<td>48</td>
<td>2</td>
</tr>
<tr>
<td>AuNP100</td>
<td>57</td>
<td>2</td>
</tr>
</tbody>
</table>

The energy barriers for deposition onto silica sand were higher for the larger AuNPs, with values for AuNP50 of \( 48 \ k_B T \) and for AuNP100 of \( 57 \ k_B T \) while for AuNP10 it was \( 6 \ k_B T \) (where \( k_B \) is Boltzmann constant and \( T \) is absolute temperature) as seen in Table 2.3.

For AuNPs aggregation, from Table 2.3 the energy barriers of the interaction energy were still higher for the larger AuNPs, with values of \( 23 \ k_B T \) for AuNP50 and \( 22 \ k_B T \) for AuNP100 compared to the lower value for AuNP10 \( (1 \ k_B T) \). When comparing the maximum energy barriers for deposition with the energy barriers for aggregation (Table 2.3), the energy barriers for aggregation were significantly lower and such reductions indicate that aggregation is more likely to occur than deposition onto sand particles. High energy barriers are indicators of high AuNPs stability, since vdW interactions are less probable to occur. In the calculations the larger AuNPs showed the higher energy barriers compared to the smaller AuNPs, but as the experiments showed, the stability was considered higher for the smaller AuNPs than for the larger AuNPs, since DLVO does not take into account the steric effects of the PEG coating on the AuNPs, and the degree of stability can also impact the interactions with silica sand.

The DLVO calculations between negatively charged surfaces predict that deposition and aggregation are unlikely to occur because (1) high primary energy barriers exists due to EDL interactions, and (2) nanoparticle secondary wells are not profound at the low ionic strength where the experiments were conducted. In addition, the AuNPs used in this study have PEG polymeric coatings grafted to the Au-core with the purpose of increasing their colloidal stability by preventing aggregation through steric hindrance [56-59]. The PEG-layers provide
a separation distance and entropic repulsion between two surfaces, since the compression of hydrated PEG layers is not energetically favorable [59].

However, deposition and aggregation were observed, and they occurred for larger AuNPs in all of the experiment, despite the DLVO prediction that larger AuNP100 should be more resistant against aggregation and/or deposition than AuNP10 because larger sizes and higher $\zeta$-potentials produce stronger repulsive forces (Figures 2.13 to 2.15). Under these unfavorable conditions, deposition of AuNPs onto silica sand observed in the batch experiments may have been a result of positively charged heterogeneities of the silica sand, including impurities such as traces of other minerals such as Al$_2$O$_3$. The SEM-EDS analysis of the silica sand used in this study showed small amounts of aluminum oxides (Figure 2.7 and Table 2.2). These heterogeneities may exist as near-neutral or positive charges in silica sand, providing favorable deposition sites for AuNPs attachment similar to previous studies [21, 60-62].

However, the presence of favorable deposition sites due to charge heterogeneities of silica sand alone cannot explain the differences in deposition and aggregation behavior of the different-sized AuNPs. Although locally attractive interactions with the charge heterogeneities may occur for the AuNPs since the energy barrier disappears, deposition was greater for AuNP100 and AuNP50 than for AuNP10.

The energy barriers for deposition predicted by the DLVO theory (Figures 2.13 to 2.15) are more significant for larger nanoparticles, thus deposition of larger AuNPs should be less for the smaller AuNPs at low IS [63-64].

One of the causes for the reversal of the DLVO predictions may be the steric interactions from the PEG layers attached on individual AuNPs. The PEG layer was 17 ± 2 nm for AuNP10, which was slightly longer, thus resulting in greater interparticle separation distance than AuNP50 (16 ± 3 nm) and AuNP100 (13 ± 8 nm) (Table 2.1). The repulsive steric stabilizing effects from the thicker PEG-layer of AuNP10 may have been more significant than the electrostatic attractions with the charge heterogeneities and may have prevented the deposition. On the other hand, lower steric stabilization imparted by the thinner PEG-layers of AuNP50 and AuNP100 may have allowed the deposition to occur. The attachment and aggregation behavior of AuNP50 and AuNP100 in the batch deposition experiments may also be a result of the thinner PEG-layer being unable to produce enough separation distances between the two
surfaces to prevent attractive interactions (i.e., electrostatic interactions or vdW forces) leading to deposition and/or aggregation. The greater degree of steric stabilization provided by the thicker PEG-coating of AuNP10 may have resulted in lower deposition and aggregation due to the increased separation distances. In addition to physical and chemical properties of AuNPs such as size and surface charge, steric interactions arising from surface coatings may potentially be one of the factors that affect the behavior of nanoparticles.

2.4.2 Effects of AuNP Interactions on Migration Behaviors

The results of the column experiments were consistent with the batch experiments that notable deposition and aggregation were observed for AuNP50 and AuNP100, but not for AuNP10. Retentions of AuNP50 and AuNP100 were approximately 12 and 15%, respectively, and LSPR peak decline, broadening, and shifting of the effluent suggested aggregation. AuNP10 was the most mobile with the maximum $C/C_0$ reaching close to 1 with almost complete recovery in the effluents (> 95 %), and small detection of aggregates.

All of the BTCs of the AuNPs produced sloped plateaus where the relative effluent concentrations ($C/C_0$) increased gradually with time, instead of flat plateaus seen in the BTC of HTO (Figure 2.10). The time-dependent deposition of sloped plateaus has been proposed to occur when particles deposit and occupy available favorable deposition sites, “blocking” or making them unavailable for further deposition [65-67]. The sloping plateaus may suggest attractive interactions of AuNPs onto limited sites favorable for deposition arising from charge heterogeneities of silica sand. The sloping plateau was also observed for AuNP10, suggesting that attractive interactions occurred between AuNP10 and silica sand, although they were weak to cause observable retention of the particles in the column.

In order to compare the affinity of AuNPs of different sizes to silica sand, the attachment efficiency ($\alpha$) was calculated using the colloid filtration theory (CFT). The attachment efficiency is defined as the probability of contacts that result in attachment. The single-collector contact efficiency ($\eta_0$) was calculated considering the contributions of interception, gravitational sedimentation and Brownian diffusion by the correlation equation proposed by Tufenkji and Elimelech [55] as follows:
For individual suspended nanoparticles, Brownian diffusion ($\eta_0$) is the dominant mechanism by which particles come in contact with the surface of the collector ($\eta_0 \approx \eta_0$) [54-55]. Since the van der Waals (vdW) force is a body force, the presence of the long PEG polymeric chains coatings on the surface of AuNPs and their impact on the value of the Hamaker constant has to be taken into account. Therefore, it is reasonable to use the Hamaker constant between silica and PEG in water as medium ($A_{PEG/H2O/Si}$) for the theoretical calculations of $\eta_0$ [55].

$\eta_0$ was calculated [55] using the following correlation Equation 2.8:

$$\eta_0 = 2.4A_S^{1/3}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{-0.052}$$

(2.8)

where $A_S$ is the porosity parameter, $N_R$ is the aspect ratio between the collector media and the AuNPs, $N_{Pe}$ is the Peclet number characterizing ratio of convective to diffusive transport and $N_{vdW}$ is the van der Waals number characterizing ratio of van der Waals interaction energy, parameters defined by the following equations:

$$A_S = \frac{2(1-y^5)}{2-3y+3y^5-2y^6} \text{ where } y = (1-f)^{1/3}$$

(2.9)

$$N_R = \frac{d_p}{d_c}$$

(2.10)

$$N_{Pe} = \frac{Ud_c}{D_{\infty}}$$

(2.11)

$$N_{vdW} = \frac{A}{k_BT}$$

(2.12)

where $f$ is the porosity of the medium, $d_p$ is the AuNPs diameter, $d_c$ is the silica sand grain diameter, $U$ is the approach velocity of fluid, $D_{\infty}$ is the diffusion coefficient in an infinite medium (determined by the Stokes-Einstein equation), $A$ is the Hamaker constant, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The Hamaker constants calculation between two materials and a medium $A_{PEG/H2O/Si}$ was based on the Hamaker constants for the vdW interactions of the materials in vacuum ($A_{PEG}$, $A_{H2O}$ and $A_{Si}$) in a third media and was calculated with Equation 2.13 [52]:

70
\[ A_{\text{PEG/H2O/Si}} = (A_{\text{PEG}}^{1/2} - A_{\text{H2O}}^{1/2}) \times (A_{\text{Si}}^{1/2} - A_{\text{H2O}}^{1/2}) \]  \hspace{1cm} (2.13)

Based on reported Hamaker values in vacuo for \( A_{\text{H2O}} \), \( A_{\text{PEG}} \) (approximate to the PEG used in this study) and \( A_{\text{Si}} \) [52- 53], the Hamaker constant \( A_{\text{PEG/H2O/Si}} \) was calculated to be \( 5.94 \times 10^{-21} \) J.

The value of \( \eta_0 \) indicates the number of collisions that takes place in the column. The attachment efficiency \( \alpha \) is determined by dividing the actual number of attachments by the number of collisions \( \eta_0 \), and it can be considered as the affinity of the particle to the collector surface per collision. The value of \( \alpha \) is 1 when interactions are favorable for deposition (i.e., vdW forces) and all the collisions result in attachment, and becomes 0 under unfavorable conditions (i.e., in the presence of repulsive interactions) when no retention occurs. In the calculation of \( \eta_0 \), “clean bed”, or the collector surface free of colloidal deposition, is assumed. The colloid deposition rate is determined only by the interactions between colloids and collector surfaces such as when colloids pass through an initially clean media, not considering a fraction of collector surface covered with deposited colloids.

The attachment efficiency \( \alpha \) was calculated with the obtained \( \eta_0 \) value with the following equation [55]:

\[ \alpha = 1 - \frac{2d_c}{3(1-f)\eta_0L} \ln \left( \frac{C}{C_0} \right) \]  \hspace{1cm} (2.14)

where \( d_c \) is the diameter of the spherical collector of the porous medium, \( f \) and \( L \) are the porosity and length of the packed porous medium, respectively. The value of \( C/C_0 \) at the middle point of the injection time of the BTCs was used for this calculation because \( C/C_0 \) did not reach an equilibrium. Other values used in the calculations are listed in Table 2.4.
Table 2.4. Parameter Values Used for $\eta_0$ and $\alpha$ Numerical Calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann constant ($k_B$)</td>
<td>$1.38 \times 10^{-23}$ J/K</td>
</tr>
<tr>
<td>Particle diameters ($d_p$)</td>
<td>43, 82 and 127 nm</td>
</tr>
<tr>
<td>Collector diameter ($d_c$)</td>
<td>0.425 mm</td>
</tr>
<tr>
<td>Approach fluid velocity ($U$)</td>
<td>$7.96 \times 10^{-5}$ m/s</td>
</tr>
<tr>
<td>Hamaker constant ($A$)</td>
<td>$5.94 \times 10^{-21}$ J</td>
</tr>
<tr>
<td>Temperature ($T$)</td>
<td>298 K</td>
</tr>
<tr>
<td>Porosity ($f$)</td>
<td>0.41</td>
</tr>
</tbody>
</table>

The attachment efficiencies ($\alpha$) were smaller than 1 and increased with increasing AuNP size (Figure 2.16), showing more affinity of larger nanoparticles to silica sand. Based on the values of $\alpha$, the column experiments also showed the significant influence of non-DLVO forces, as DLVO predicts more deposition and aggregation of smaller particles. One of the non-DLVO forces may be the steric stabilization imparted by the PEG layers as discussed previously. The aggregation of the larger AuNPs may have occurred due to the attachment of multiple particles onto one deposition site on silica sand followed by detachment as aggregates.

![Figure 2.16. AuNPs Experimental Attachment Efficiency ($\alpha$)](image)

Calculated experimental attachment efficiencies for the AuNPs as a function of AuNPs size.
Alternatively, it is also possible that the increase in the attachment efficiencies for larger AuNPs was caused by aggregated AuNPs remaining trapped in the porous media by physical straining and/or by remaining attached to the sand surfaces by electrostatic interactions or other physicochemical forces, while a fraction of smaller aggregates is mobilized through the column and detected in the effluents (Figures 2.12, b and 2.12, c) as has been suggested in a previous study [22].

The results from the column experiments confirmed the batch results that non-DLVO forces may be affecting the deposition and aggregation behaviors, thus mobility of AuNPs. These non-DLVO forces may include the repulsive steric stabilizing effects arising from the surface coating of the nanoparticles. In the subsurface environment where radioactive waste disposal facilities are/will be placed, natural organic matter (NOM) may be present, which may attach to the surface of colloids/nanoparticles to play a role in stabilizing them similar to polymeric surface coatings. Non-DLVO forces, including steric effects, are not yet fully incorporated in the modelling of colloidal transport.

Our results suggest the importance of further understanding of non-DLVO colloidal interactions and the development of more reliable transport models.

2.5 Conclusions

Batch deposition and column transport experiments were conducted using AuNPs of three different sizes in order to investigate the effects of colloidal properties on their migration behaviors. Our findings are as follows:

- Deposition and aggregation were mainly observed for larger AuNPs from both the batch and the column experiments, despite the predictions from the DLVO theory that smaller nanoparticles are more likely to show deposition and/or aggregation. This result may imply the importance of non-DLVO interactions.

- Occurrence of deposition despite the unfavorable conditions of both AuNPs and silica sand having overall negative surface charges may be a result of charge heterogeneities of silica sand. The sloping plateaus observed in the BTCs of AuNPs in the column experiments may
support the existence of a limited number of sites that exhibit attractive interactions with AuNPs.

One of the possible non-DLVO interactions that may be important in our experimental system is steric effects imparted by the PEG layer. The thinner PEG layer of the larger AuNPs may have been unable to maintain long enough separation distance for attractive interactions to result in deposition and aggregation, whereas the thicker PEG-layer of AuNP10 may have been able to stabilize them against deposition and aggregation. In addition to the characteristics of AuNPs such as particle size and surface charge, properties of the surface coating, including steric effects, may play a significant role in controlling the AuNPs stability and deposition, thus affecting migration behaviors.

These results may have important implications on the safety assessment of HLW repositories because natural organic matter (NOM) in the natural subsurface environment may attach to the surface of colloids/nanoparticles and modify the migration behavior. Further studies on non-DLVO forces, including steric effects, are necessary to fully understand and to incorporate the interactions in the modelling of colloidal transport.
References


27. Lee JS, Han MS, Mirkin CA. Colorimetric detection of mercuric ion (Hg^{2+}) in aqueous media using DNA-functionalized gold nanoparticles. Angew Chem Int Ed. 2007;46:4093-4096.


Chapter 3. Deposition Behavior of Gold Nanoparticles onto Surfaces of Silica Sand
3.1 Introduction

Understanding of colloid transport in geomedia has gained great importance in recent years since several reports have shown that colloids can enhance the migration of different contaminants with low solubility such as heavy metals [1-2]. Transport of insoluble contaminants occurs in groundwater when these contaminants are attached to colloidal particles. Colloid mediated transport is especially important in the performance assessment of deep geological repositories due to potential impacts on migration of radionuclides [3]. When radionuclides are attached to colloidal particles, the fate of colloidal particles affects the migration behavior of radionuclides attached to them. Migration of colloidal particles are strongly influenced by the surface interactions between colloids themselves, which may result in aggregation, and with the collector surfaces such as geomedia, which may result in deposition. The study on surface interactions of colloidal material and nanoparticles (NPs) in porous media can help understand the impacts of aggregation and deposition of colloids on their mobility, fate and persistence in the environment [4].

Colloidal interfacial interactions are typically modelled by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [4-6] which considers the attractive van der Waals (vdW) and repulsive electrostatic forces. However, there are observations from deposition studies using model colloids on well-defined collector surfaces that showed discrepancies from the theoretical predictions [7]. The poor agreement has been attributed to non-DLVO forces such as surface roughness of the collector surfaces [8], steric interactions, H-bonding, hydrophobic effect, hydration pressure, Lewis acid-base interactions [9]. Although progresses have been made to correct the deviations between the DLVO theory and experimental results including the proposition of the extended DLVO (XDLVO) theory [10], none so far can universally predict migration behaviors of colloids under various conditions. A better understanding of the processes involved in deposition and aggregation of colloidal particles is essential in order to develop improved transport and/or deposition models [11-12].

In Chapter 2, transport experiments were conducted with aqueous solutions of polymer coated gold nanoparticles (AuNPs) with different sizes in a column packed with silica sand. The results suggested that deposition and aggregation of AuNPs occurred in the column, and they were more significant for larger AuNPs. Both deposition and aggregation of AuNPs were also observed in batch experiments in the presence of silica sand, and they were significant for
larger AuNPs as well. The behavior of colloids inside a water saturated porous medium is considered to be mainly controlled by the interparticle forces or colloidal interactions, which produce deposition if the colloid-collector interactions are attractive [13]. In the experiment described in Chapter 2, deposition on silica sand was not expected because both AuNPs and silica sand have negatively charged surfaces. In addition, DLVO theory predicts less attractive interactions for larger AuNPs.

A potential cause for the observed deposition may be the presence of metal oxides such as iron or aluminum oxides as accessory minerals. They can have positively charged surfaces [14] and can favorably attract and destabilize AuNPs. However, charge heterogeneity on silica sand does not cause more deposition and aggregation of smaller AuNPs. The energy barriers calculated by DLVO theory are higher for larger AuNPs. The results suggested potential role of charge heterogeneity on silica sand, and possible significance of non-DLVO forces, but the detailed mechanisms of deposition and aggregation were not clear.

To further understand the deposition mechanisms of AuNPs onto silica sand, silica sand particles after batch experiments were observed using scanning electron microscope (SEM) and SEM-energy dispersive X-ray spectroscopy (SEM-EDS) to relate surface morphology and chemical composition of silica sand with AuNP deposition. This study aims to identify the factors that lead to destabilization, deposition and/or aggregation of AuNPs by examining the interactions between the AuNPs and the silica sand in relation to mineral composition, overall surface charges, localized charge heterogeneities, and surface morphologies. The results of this work can improve the understanding of the mechanisms of colloidal transport in porous media, which is expected to contribute to improvement of accuracy and confidence in safety assessment of geological disposal.

3.2 Materials and Methods

3.2.1 Gold Nanoparticles (AuNPs) and Silica Sand

Stock solutions of spherical gold nanoparticles with different nominal core sizes of 10, 50 and 100 nm (AuNP10, AuNP50 and AuNP100, respectively) were purchased (NanoComposix, NanoXact, USA) and were used after dilution with deionized (DI) water. The AuNPs are reported to have a coating of poly (ethylene glycol)-methyl thiol (PEG) as the provided data
showed. The AuNPs suspensions were kept and stored in the dark at 5 °C and were vortexed and/or sonicated before the experiments. Albany silica sand quartz grains (99.8% SiO\(_2\), Tochu, Japan,) of high purity with average particle size of 0.425 mm were used in this study.

3.2.2 Characterization Methods of the AuNPs and Silica Sand

Detailed characterization procedures for AuNPs were previously described in Chapter 2. Briefly, they were analyzed by transmission electron microscope (TEM), dynamic light scattering (DLS) and zeta-potentials (ζ-potentials). The AuNPs UV-Vis spectra were obtained (Hitachi U-5100, Japan) to confirm the localized surface plasmon resonance (LSPR) bands of the AuNPs in order to quantify their concentrations.

The zeta-potential (ζ-potentials) of silica sand particles was analyzed by electrophoretic light scattering (ELS) (Delsa Nano HC, Beckman Coulter, USA). Sand particles were first thoroughly washed with DI water, then sonicated for 5 minutes in DI water and fluid samples were used to measure the ζ-potentials in a way similar described in Li et al [11].

Scanning electron microscopy (SEM) image analyses (JEOL, JSM-7001FA, Japan) were conducted for the silica sand samples to observe the features of their surface morphology such as roughness, cavities and fractures, and to observe depositions of the AuNPs onto the sand surfaces. SEM samples were prepared by drying the silica sand grains overnight at room temperature, and later attaching them to brass stubs using carbon tape. They were sputter-coated (Vacuum Device VC-100 Carbon Coater, Japan) with a thin carbon coating. Analysis by the EDS was carried to determine the elemental composition of the sand surfaces and to confirm the presence of AuNPs.

3.2.3 Batch Experiments

Batch experiments were conducted to examine the AuNPs deposition (attachment) behavior on the silica sand surfaces as in Chapter 2. The tubes were mixed after the addition of AuNP10, AuNP50, and AuNP100 solutions. The suspensions of AuNPs and silica sand were gently mixed at room temperature for 1 h while shielded from ambient light. Afterwards, the supernatant solutions were decanted, and the sand grains were removed and vacuum-dried at room temperature overnight. Randomly selected sand grains from each deposition experiment
were used for SEM analysis. Figure 3.1 illustrates the AuNPs nanoparticle deposition experiments setup and sample preparations carried out for the SEM and SEM-EDS analyses.

Figure 3.1. Schematic Illustration of the Experiments Used for SEM Observations

3.3 Results

3.3.1 Silica Sand Morphological and Chemical Properties

Silica sand samples were examined to obtain information of their morphological and chemical characteristics. Randomly selected sand grains were mounted for SEM visual observation at various magnifications and EDS measurements. Figure 3.2 shows an example of SEM images. Silica sand particles were found to be mostly long rounded grains with a mean diameter of ~0.425 mm (Table 2.2). Furthermore, discernible irregularities such as cavities or fractured and abraded surfaces were observed on the sand surfaces as Figures 3.3 and 3.4 show at increased magnifications.
Figure 3.2. SEM Silica Sand Particles Image at 25X

Figure 3.3. SEM Silica Sand Surface Morphology Image at 3000X
EDS analyses of the silica sand surfaces were carried to obtain information for the minerals present on the surfaces since they can affect the interaction behavior with other particles such as AuNPs used in this study. The chemical composition of silica sand provided by the manufacturer (Table 2.2) showed that the main component is SiO$_2$ with the presence of other accessory minerals, mainly metal oxides such as Al$_2$O$_3$, Fe$_2$O$_3$, MgO and TiO$_2$. The elemental composition found on the surface of the silica sand was investigated by EDS color mapping (Figures 3.5) and obtaining compositions of random areas. The results are summarized in Table 3.1 from the analysis of 6 areas of different sand particles. The composition observed by EDS was similar to Table 2.2.

Table 3.1 Silica Sand EDS Elemental Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>(weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>99.32 ± 0.20</td>
</tr>
<tr>
<td>Al</td>
<td>0.07 ± 0.08</td>
</tr>
<tr>
<td>Fe</td>
<td>0.22 ± 0.11</td>
</tr>
<tr>
<td>Na</td>
<td>0.08 ± 0.07</td>
</tr>
<tr>
<td>Mg</td>
<td>0.04 ± 0.04</td>
</tr>
<tr>
<td>Ti</td>
<td>0.27 ± 0.16</td>
</tr>
</tbody>
</table>
Trace amounts of accessory minerals on the surface of random silica sand grains were also identified locally by SEM-EDS, as shown in Figures 3.6 and 3.7. The presence of these accessory minerals was random; however, they were often detected near rough areas or inside cavities or fractures found on the sand surfaces. For example, in Figure 3.6 one Al particle of ~2 μm was found in the edge of a cavity. In Figure 3.7 the Al and Na observed are probably from clay coatings commonly found inside cavities of sand grains [1]. These elements detected as accessory minerals were similar to the elements that are included as the composition of the silica sand shown in Table 2.2.
Figure 3.6. EDS Elemental Color Mapping Results for the Selected Area of the Silica Sand

Aluminum particles shown inside a white circle.
The zeta-potential of silica sand was measured by DLS, which showed that sand is negatively charged at \(-32 \pm 0\) mV in DI water under the experimental conditions of this study. The Point of Zero Charge (PZC) of silica has been reported to be \(~3.5\) [1], and this result is consistent with the chemical composition obtained that silica sand consists mainly of SiO\(_2\) and with reported values shown in Table 2.2. The zeta potential results indicate that the sand grains were overall negatively charged, although small accessory minerals may pose localized positive charges (Table 3.2).

3.3.2 AuNPs Deposition Observed by SEM-EDS

The characteristics of AuNP10, AuNP50 and AuNP100 particles are shown in Chapter 2, and summarized in Table 2.1. The presence of deposited AuNPs on the surfaces of the silica sand grains was confirmed by EDS analyses on selected areas. Visible AuNPs were observed as in Figures 3.8, 3.9, and 3.10. The elemental analyses of the areas in Figures 3.8, 3.9, and 3.10 are shown in Table 3.2. and the presence of AuNPs was confirmed.
Figure 3.8. SEM Image of AuNP10 with EDS Spectra
EDS spectra for a selected area with AuNP10.

Figure 3.9. SEM Image of AuNP50 with EDS Spectra
EDS spectra for a selected area with AuNP50.
Randomly selected silica sand grains after deposition of AuNP10 were studied by SEM as shown in Figure 3.11. Deposited AuNP10 particles were found in an area with minimal roughness compared to other regions of the silica sand surfaces, as seen in Figure 3.11, top left. At higher magnifications shown in top right and bottom in Figure 3.11, AuNP10 particles were seen with good resolution and they were randomly distributed. In addition, they were
deposited as single particles with no observable aggregation. This was consistent from at least 25 images taken in more than 10 different regions of a silica sand grain *(Appendix A)*.

Figure 3.1. Typical Silica Sand SEM Images for the Observation of AuNP10 Particles

SEM images of silica sand surfaces taken after the deposition experiment.

The SEM examinations for the deposition of AuNP50 *(Figure 3.12)* showed a different behavior than what was obtained for AuNP10 *(Figure 3.11)*. Deposition of AuNPs were found more often (deposition observed on 4 grains out of 8 grains analyzed) than AuNP10 (deposition observed on 1 grain out of 8 grains analyzed). The nanoparticles were deposited on the sand surfaces, often in rough regions such as fractures and cracks, as presented in *Figure 3.12*, top left. At higher magnifications and resolution as shown in *Figure 3.12*, top right and bottom, it was revealed that the AuNP50 were deposited as aggregates of doublets, triplets, and clusters, as well as single particles. This was observed consistently in more than 20 images taken in different grains and different regions *(Appendix B)*.
Figure 3.1. Typical Silica Sand SEM Images for the Observation of AuNP50 Particles

SEM images of silica sand surfaces taken after the deposition experiment. Arrows indicate AuNPs aggregates.

Micrographs obtained from the SEM analysis of AuNP100 (Figure 3.13) showed a deposition behavior similar to AuNP50 (Figure 3.12). The AuNP100 were deposited onto the silica sand surfaces in the vicinity of irregular or rough regions such as fractures and cracks. This was consistent after the observation of 10 silica sand grains. At high magnifications as shown in Figure 3.13, top right and bottom indicate that the AuNP100 particles were distributed as aggregates as well as single particles. This was also consistently seen in at least 20 images taken from different grains and regions (Appendix C). The degree of aggregation was more significant for AuNP100 with more clusters than doublets and triplets.
Figure 3.13. Typical Silica Sand SEM Images for the Observation of AuNP100 Particles

SEM images of silica sand surfaces taken after the deposition experiment. Arrows indicate AuNPs aggregates.

SEM-EDS elemental color mapping for the areas where AuNPs were observed deposited were also obtained and representative results from five different measurements in different areas of different sand particles (except for AuNP10) are showed in Figures 3.14, 3.15 and 3.16 for AuNP10, AuNP50 and AuNP100 respectively.

The deposition of the AuNPs was observed and confirmed by the higher intensity of Au colored areas and in the peaks of the spectra for the different AuNPs in Figures 3.14, 3.15 and 3.16, and the presence of secondary minerals was also observed by color intensity and peak in the spectra in the analyzed areas similarly as in Figures 3.15 and 3.16. However, in the case for the EDS mapping of AuNP100 increased amounts of other secondary minerals such as Fe and/or Ti were detected, as shown in Figure 3.16 and it was also observed that the majority of
the AuNP100 particles were not found to be directly deposited on top of these minerals but mainly in the nearby rough areas (Figure 3.16) similarly as AuNP50.

Figure 3.14. SEM-EDS Elemental Color Mapping, Concentration (weight %) and Spectra for an Area with AuNP10 Particles
Figure 3.15. SEM-EDS Elemental Color Mapping, Concentration (weight %) and Spectra for an Area with AuNP50 Particles
3.4 Discussion

3.4.1 AuNPs Deposition Behavior onto Silica Sand

Silica sand is an example of the simplest geological medium. There are other much more complex and heterogenous materials in both physical and chemical properties [15]. Thus, the first step towards understanding the mechanisms of colloidal transport in geological media is
to elucidate the interactions of silica sand with other particles and to identify the properties of the sand that control the transport of particles.

Silica sand is mainly composed of SiO\(_2\), which has an overall negative zeta potential. Because AuNPs also has negatively charged surfaces as shown in Table 2.1, the deposition of AuNPs on silica sand should be hindered by repulsive electrostatic forces according to the DLVO theory estimations (Figures 2.13 – 2.15). SEM images of silica sand after batch deposition experiments (Figures 3.11, 3.12 and 3.13) showed that only small and limited areas of the silica sand surfaces were covered by the AuNPs particles. This overall hinderance against deposition was consistent with the DLVO theory that predicts minimal interactions of AuNPs with silica sand surfaces, however accessory or secondary minerals can produce positive charges where deposition can occur [11].

Deposition of AuNP10 was observed to be dispersed on a smoother region of a silica sand grain (Figure 3.11), whereas deposition of AuNP50 and AuNP100 (Figures 3.12 and 3.13) was often observed near rough surfaces. EDS analyses of silica sand showed the presence of secondary minerals (Figures 3.6 and 3.7). Some of this mineral heterogeneity was observed more in areas of sand that had rough surfaces such as cavities and cracks. This observation is consistent with the understanding that weathering of minerals like silica sand produces coatings of clay and/or mixed oxides of various kinds, and in open cavities (rough areas) they may be filled with these clays and/or other minerals [16]. Recent observations suggested that the cavities on the surfaces of quartz sand particles were filled with oxides of aluminum and potassium [11]. A similar behavior was observed especially in the rough areas near to where AuNP100 deposited and where significant Fe and/or Ti fractions as the observed in Figure 3.16 were detected. The deposition of AuNPs (Figures 3.14 – 3.16) may be influenced by interactions with these or other kind of secondary minerals which are unable to detect by EDS analyses (i.e., microscale order), however only a limited direct deposition to these secondary minerals was observed (Figure 3.16).

Another possibility is the physical influence of the surface roughness on the AuNPs deposition since localized hydrodynamic shear disturbances can occur on the rougher areas [11]. The influence of surface roughness on particles deposition is still unclear, however it has been proposed that particles can remain attached not only by surface roughness effects but in combination with the effects of attractive DLVO interactions [17]. It is possible that the
combined effects of the charge heterogeneities and surface roughness produced the AuNP50 and AuNP100 deposition detected near cavities and rough areas (Figures 3.12 – 3.13 and Figures 3.15 – 3.16).

The results showed that deposition was more significant for larger AuNPs, and they deviate from the DLVO calculations that deposition of smaller AuNPs is more likely (Table 2.3). It is possible that non-DLVO interactions were modulating the colloidal interactions between the AuNPs and the silica sand surfaces physicochemical heterogeneities and producing the deviations with DLVO. In the system evaluated, one of the relevant non-DLVO effects may be attributed to the PEG repulsive steric stabilization as discussed in Chapter 2. The thicker PEG layer of AuNP10 may hinder DLVO attractive interactions between the AuNPs and the surface heterogeneities more than AuNP50 and AuNP100.

3.4.2 AuNPs Aggregation Behavior

An increased aggregation was detected for AuNP50 and AuNP100 (Figures 3.12 and 3.13), whereas aggregation was minimal AuNP10 (Figure 3.11). In addition, aggregation was more significant for AuNP100 than for AuNP50, producing more clusters than doublets or triplets. Observation of aggregated AuNPs by the SEM analyses may suggest that the attraction between deposited-AuNPs and suspended-AuNPs likely occurred. In the column experiments discussed in Chapter 2, sloping plateaus in the breakthrough curves were observed. This time-dependent deposition exhibiting sloping plateaus has been proposed to occur when particles deposit and occupy available favorable deposition sites, making these sites unavailable, or “blocking” them from further deposition [19-21]. Attractive interactions suggested by formation of aggregates on silica sand surfaces observed by the SEM analyses may support the attractive interactions of AuNPs onto limited sites favorable for deposition observed in column experiments.

The results showed more aggregation of larger AuNPs and they were not consistent with the DLVO calculations (Table 2.3). Similar to deposition, this may have been caused by the PEG repulsive steric stabilization as discussed in Chapter 2.
3.5 Conclusions

Silica sand surfaces after deposition experiments with AuNPs were observed by SEM and analyzed by SEM-EDS in order to elucidate the mechanisms for deposition and aggregation in relation to surface interactions. Deposition of AuNPs onto silica sand surfaces occurred, but only in small areas, which was consistent with the predictions from DLVO theory that overall deposition is not expected due repulsive interactions between AuNPs and silica sand. All of the AuNPs of different sizes showed deposition: it was significant for AuNP50 and AuNP100. Deposition for AuNP50 and AuNP100 occurred more in the rough surfaces of the silica sand. This may suggest that charge heterogeneity caused by the presence of secondary minerals may influence the deposition behavior. Another possibility are the physical effects and the local hydrodynamic flow disturbances in these rough surfaces. From the SEM-EDS observations, it was not possible to discuss and compare the significance of these two effects. Mechanisms for the deposition of AuNP10 may be different because AuNP10 was deposited dispersed on a smoother area of the silica sand.

Aggregation was also directly observed by SEM for AuNP50 and AuNP100, but minimal for AuNP10. Degree of aggregation was more significant for AuNP100 with more clusters observed than AuNP50 that showed more pairs and triplets. Stronger interactions were suggested for larger AuNPs for both between the surfaces of AuNP and silica sand, and between AuNPs. These observations may suggest the significance of non-DLVO interactions. One possibility of the non-DLVO force that may have been significant in the system is steric effect as discussed in Chapter 2.

Classical colloidal theories model colloidal interactions in a system composed of smooth and homogeneous particles as collectors. However, even a simplified system consisting of silica sand showed significant discrepancies from theoretical predictions. This study identified some of the factors that may influence the migration behavior of colloidal particles: charge heterogeneity on collector surfaces, surface roughness of the porous media, and steric effects of the colloidal particles. In natural environment, great heterogeneities such as sizes and chemical compositions exist. In order to reliably predict the fate and transport of radionuclides attached to colloids for the safety assessment of HLW geological disposal facilities, further
study is necessary to evaluate the effects of heterogeneities on geological media as well as colloidal particles.
References


Chapter 4. Interaction Behavior of Gold Nanoparticles with Engineered Barrier Material Particles
4.1 Introduction

Deep geological disposal of high-level radioactive waste (HLW) which contains high concentrations of long-lived radionuclides [1] is considered to be the most safe and reliable method [2]. In many countries including France, Belgium and Switzerland the HLW geological disposal facilities will be equipped with multi-barrier or engineered barrier systems designed to isolate and contain HLW for several hundreds or thousands of years [3-9] before it can reach the biosphere [2].

The multibarrier systems may be different depending on the design of a repository [2] however they will consist in natural (host rock) and engineered barriers. The engineered barriers will be composed of different components including the waste form, waste containers and buffers or backfills [2]. The buffer material is a key element in the multibarrier system since it will be responsible of containing leaching radionuclides once groundwater comes in contact with the isolated HLW radionuclides [10].

In Japan, a candidate buffer material is compacted bentonite, a type of clay where the major mineral is montmorillonite. Sodium and calcium bentonite are the most common montmorillonite varieties, of which sodium bentonite shows lower hydraulic conductivity, thus its application is more beneficial in hydraulic containment applications [11]. In an HLW repository, compacted bentonite such as sodium montmorillonite (Na-montmorillonite) will be loaded around the containers containing the waste to also enhance the repository long-term stability [12].

Montmorillonite is a 2:1 clay type consisting of a mixture of minerals with a sheet-like structure with nanometer thickness (~ 1 nm), described chemically as hydrous aluminum silicate that consists of two tetrahedral sheets of Si separated by one octahedral sheet of Al (formation of TOT layers) [13-14].

There is possibility that the tetravalent Si$^{4+}$ in the tetrahedral sheet or the Al$^{3+}$ in the octahedral sites are replaced by divalent Fe$^{2+}$ or Mg$^{2+}$ cations or naturally occurring with Na$^{+}$ and Ca$^{2+}$, known as isomorphous substitution, resulting in a deficiency of positive charges, thus producing a net negative surface charge [5, 14].
Adjacent montmorillonite particles can produce “card-house” microstructures due to their proximity which can produce bonds as a result of electrostatic attractions between the negative surface faces with the positive edges [15].

Possible interactions of montmorillonite are due to chemical heterogeneities found on the montmorillonite sheet particles or platelets since they can develop positive surface charges at pH values lower than the point of zero charge (PZC) of the montmorillonite edges, since at the edges of the montmorillonite the Si-Al structures become exposed since their structure breaks producing Si-OH and Al-OH amphoteric groups [8] or due the presence of cation-exchange capacity sites [5, 14].

Clay mineral edges such as in montmorillonite carry very little oxide-type groups that can dominate adsorption of trace metals and/or organic molecules under some conditions [16]. Simple oxide minerals (such as Al₂O₃) have a reactivity that is influenced by changes in pH through the following type of reaction [16]:

\[ >\text{SOH}_n \leftrightarrow >\text{SOH}_{n-1} + H^+ \]

where \( >\text{SOH}_n \) is a generic surface charge and the equation shows that a variable net proton density is dependent on pH and IS [16]. Other studies have reported that the edges surface charge (zeta-potential) will be related to the silica (SiO₂) and alumina (Al₂O₃) and that can also be influenced by isomorphic substitutions of Si by Al and of Al by Mg, Fe²⁺ or Fe³⁺ [17].

These chemical and physical properties shown by montmorillonite are responsible for the many functions including low diffusion properties and strong sorption capacity [18] which are of high importance in the engineered barriers of HLW repositories. Since it has been recognized that montmorillonite buffer material is key in reducing the mobility of radionuclides in multi-barrier systems [2], thus improving the understanding of radionuclides migration behavior in montmorillonite is important for the safety assessment of HLW repositories.

The migration of radionuclides has been considered to be mainly controlled by their sorption to the soil or rock matrix [19]. Insoluble radionuclides or radionuclides that were sorbed easily were considered to be immobile because they were removed from the mobile phase (liquid or gas) [19]. This was the case for Pu, Am, Eu, Cs and Sr because they have very low solubility.
or they sorb quickly to the solid phases (i.e., soil) it was thought that they would not be transported [19].

However, recent studies [19-20] began contradicting this idea since radionuclides considered to be immobile were detected at long distances from the sources and this was attributed to naturally existing mobile colloids present in groundwaters acting as carriers and enhancing the transport of radionuclides [19-20] known as colloid facilitated transport.

Colloid facilitated transport can be possible if low solubility and readily sorbed radionuclides attach to the colloid material [19-20]. For example, a treated waste stream containing Am was liberated from into a canyon at Los Alamos National Laboratory and Am was detected more than 3 km away from the original source strongly attached with colloids in the 25 to 430 nm size range [19].

Furthermore, field experiments performed at the Grimsel Test Site (GTS) in Switzerland showed that when radionuclides sorbed onto bentonite colloids were injected in a fractured shear zone, the majority of the Am and Pu migrated without retardation when associated with colloids [21].

The experimental evidence [19-20] is showing that colloidal facilitated transport is very important for the safety assessment of HLW repositories since it can change the migration behavior of dissolved radionuclides. However, although the current understanding of colloidal facilitated transport has advanced considerably, it is still not sufficient to effectively develop a single transport model able to predict the migration behavior of radionuclides in underground systems.

One of the greatest challenges of studying colloidal transport, is that determining the relevant interactions controlling the migration of colloids in natural systems is very difficult to study because they have large chemical and physical heterogeneities (i.e., compositions, sizes and shapes) [22] that are difficult to analyze, thus reducing the ability to determine the important individual factors and/or processes or to predict their interaction behavior using the Derjaguin-Landau-Verwey-Overbeek (DLVO) [23].
To study colloidal transport in soil minerals, gold nanoparticles (AuNPs) can be useful because they are stable and have physicochemical properties that are easy to detect and to customize (i.e., size and surface coating) to have different sizes or known properties [24], making them good candidates to be used as model colloids.

In the previous chapters, different-sized AuNPs with a polymeric coating were used to understand the interactions with silica sand particles in batch and transport experiments in order to elucidate the processes that affect their deposition and transport behavior. The presence of charge heterogeneities was found to impact the attractive interactions between the AuNPs with the silica sand surfaces. Herein we use the same AuNPs in batch experiments with sodium montmorillonite (Na-montmorillonite) particles since in the edge possible attractive interactions with AuNPs can occur due to charge heterogeneities and can help to improve the understanding of how natural colloids can interact with Na-montmorillonite.

The purpose of this work is to investigate the interactions that can affect the sorption behavior between the heterogeneous mineral surfaces of Na-montmorillonite particles and polymer-coated AuNPs that were used as model or surrogate natural colloids in batch experiments under low pH conditions. Recent evidence of uncoated or “bare” silver and gold nanoparticles sorption to clay minerals [23, 25] suggested that nanoparticles become destabilized and attach and/or aggregate significantly onto the edge faces of the clays at low pH values (pH < 4), below the point of zero charge (PZC) of the edge faces.

However, this has not been tested for polymer-coated gold nanoparticles (AuNPs) such as the PEGylated AuNPs used. Batch experiments in the presence of different concentrations of different sized AuNPs were performed and the obtained samples were examined for the presence of attachments and/or aggregation by UV-Vis, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS).

Understanding how the sorption of colloids or nanoparticles to soil minerals occurs is important because they can affect colloids transport and of the associated contaminants. These is of high importance for the safety assessment of deep geological repositories, where the understanding of the interactions between colloids or nanoparticles with clay particles is critical since colloids can enhance the transport of radionuclides by mobilizing together.
4.2 Materials and Methods

4.2.1 Gold Nanoparticles (AuNPs) and Na-montmorillonite

AuNPs solutions of different nominal spherical Au-core sizes of 10, 50 and 100 nm (AuNP10, AuNP50 and AuNP100, respectively) were purchased (NanoComposix, NanoXact, USA) with stock concentrations of 52, 54 and 52 mg/L, respectively. The AuNPs have a coating of poly(ethylene glycol)-methyl thiol (PEG) of ~ 5 kDa as reported by the manufacturer. AuNPs suspensions were kept and stored in the dark at 5 °C and were vortexed or sonicated before conducting the experiments.

Details of the methods for AuNPs characterizations were previously described in Chapter 2. Briefly they were characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), and the results are summarized in Table 2.1. The UV-Vis absorption spectra of AuNPs and Na-montmorillonite were obtained (Hitachi U-5100, Japan) to detect the bands of the localized surface plasmon resonance (LSPR) or absorbance maxima to determine the concentration of AuNPs, and also to observe any spectral changes due to the interactions between the AuNPs and the Na-montmorillonite particles.

Commercially available bentonite (Kunipia-F, Japan) of high montmorillonite content (reported content > 95%) was used for this study. It treated following a procedure described in Kozaki et al [26] to obtain homo-cationic Na-montmorillonite with narrow particle size distribution. Transmission Electron Microscopy (TEM) imaging was performed to observe the morphology of Na-montmorillonite (JEOL JEM-2010, Japan) with an electron microscope operating at a 200-kV accelerating voltage.

4.2.2 Batch Experiments

Batch experiments were conducted to examine the deposition behavior of AuNPs onto Na-montmorillonite particles. The outline of the batch experiments is illustrated in Figure 4.1. In the experiments, ~ 10 mg of Na-montmorillonite was suspended in 100 mL of DI water. The pH of the suspension was adjusted to ~ 3 by the progressive addition of 0.1 M HCl while continuously stirring. The pH measurements were performed with a pH meter (Horiba LAQUA F-72, Japan). Aliquots of 10 mL from the pH adjusted Na-montmorillonite suspension were
placed in 50 mL Corning centrifuge tubes. To the tubes, solutions of AuNP10, AuNP50 and AuNP100 were added to make the final concentrations of 5, 0.1 and, 0.05 mg/L. The suspension of the mixture of AuNPs and Na-montmorillonite were vortexed shortly, then gently mixed at room temperature for a time period of 24 hours on an oscillating tube shaker working at ~ 80 min⁻¹ (Water bath / Shaker, Taitec Co., Japan). The tubes were shielded from ambient light while mixing. Blank samples were prepared to follow the same procedure as described.

After mixing for 24 hours, the suspension was sampled for SEM and SEM-EDS analysis with and without washing treatment: the first procedure (without washing) was to simply disperse the suspension samples ultrasonically for 10 min before sampling a droplet for SEM analysis. The second procedure was to wash and remove the excess AuNPs and AuNPs weakly associated with Na-montmorillonite. The suspension was centrifuged for 5 min at 10,000 rpm (equivalent to 12,000 g) to sediment the Na-montmorillonite fractions of > 2 µm from the suspension [27]. Then the supernatant was decanted and replaced by pH 3 water, and vortexed for a short period of time. The washing procedure was repeated twice before the suspension was dispersed ultrasonically for 10 min, then a droplet was sampled for SEM analysis.
4.2.3  AuNPs and Na-montmorillonite Characterization Methods

The samples were mounted on holders following a method developed for clay particles [28] but was slightly modified due to the differences in experimental conditions (i.e., low pH). A small droplet of the suspension was carefully placed on top of carbon tape. The excess suspension was removed with filter paper after leaving the sample to stand for 20 min. Then the samples were air-dried overnight.

Scanning electron microscope (SEM) images were obtained (JEOL, JSM-7001FA, Japan) for the mixture samples of AuNPs and Na-montmorillonite at an accelerating voltage of 15 kV. Energy dispersive X-ray Spectroscopy (EDS) was carried in order to determine the chemical composition to confirm the presence of Na-montmorillonite particles in different regions of the samples and to confirm the presence of AuNPs.
4.3 Results

4.3.1 Properties of AuNPs and Na-montmorillonite

The AuNPs used in this study were previously characterized and the properties are summarized in Table 2.1. The ζ-potentials of the AuNPs were negative with values of -12 ± 0, -31 ± 1, and -25 ± 4 mV for AuNP10, AuNP50, and AuNP100, respectively. Solutions of AuNPs show the UV-Vis spectra as shown in Figure 2.4. The strong peaks in the visible light range correspond to the localized surface plasmon resonance (LSPR) effect.

Figure 4.2 shows a TEM image for a Na-montmorillonite sample. The TEM image shows sheet-like microstructure and morphology of Na-montmorillonite particles including the typical structures resembling lenticular pores [29]. The particle morphology and sizes in Figure 4.2 are observed to be the particles lengths in the range of 100 to 500 nm and width of ~ 1 nm, which are similar to previous reports [6, 10, 14].

Figure 4.3 shows the elemental composition for Na-montmorillonite surface obtained by TEM-EDS. In Figure 4.4 a representative elemental composition spectrum obtained by SEM-EDS for a selected area of the Na-montmorillonite is shown. The TEM-EDS shows that the main components were Si, Al, and Na, and the SEM-EDS shows they were Si, Al, Mg, and Na. These results were in agreement with the chemical composition provided by the manufacturer [10] shown in Table 4.2, showing that the main components were Si and Al, with small amount of Fe, Mg, and Na.
Figure 4.3. Na-montmorillonite TEM-EDS Spectra

Figure 4.4. Na-montmorillonite SEM-EDS Spectra

Table 4.1 Montmorillonite Chemical Composition

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Kunipia-F* (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>58.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.9</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.2</td>
</tr>
<tr>
<td>MgO</td>
<td>3.4</td>
</tr>
<tr>
<td>CaO</td>
<td>0.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.8</td>
</tr>
</tbody>
</table>

(as provided by Kunimine Industries Co.) *
4.3.2 UV-Vis Spectra of AuNPs and Na-montmorillonite Systems

The UV-Vis absorption spectra were obtained for the mixture of Na-montmorillonite and water. UV-Vis spectra changed with time, so the mixture was analyzed immediately after it was prepared and after 24 hours of mixing as shown in Figure 4.5. From the spectra, it can be seen that the Na-montmorillonite has minimal absorption in the visible light range, however a strong absorption was observed at ~ 243 nm, which is consistent with previous observations (between 241 - 243 nm) [30-31]. The peak became sharper and slightly higher after mixing for a period of 24 hours (Figure 4.5). The UV-Vis spectrum was different for the centrifuged Na-montmorillonite samples after mixing for 24 hours: the peak at ~ 243 nm disappeared, and a small peak at ~ 266 nm appeared. This was probably due to the sedimentation of a certain fraction of Na-montmorillonite by centrifugation [27].

![UV-Vis spectra for Na-montmorillonite obtained at different times.](image)

**Figure 4.5. Na-montmorillonite UV-Vis Spectra**

UV-Vis spectra for Na-montmorillonite obtained at different times.

The initial pH of the Na-montmorillonite mixed in DI water was ~ 7, and it was used after adjusting to pH 3 with 0.1 M HCl. For deposition of AuNPs onto montmorillonite, AuNPs solutions were added and mixed for 24 hours. The pH remained unchanged (pH ~ 3) and the suspensions showed the red color characteristic of AuNPs, indicating that some AuNPs may have remained in solution and/or that they could have interacted with Na-montmorillonite. The AuNPs of three different sizes were mixed to make final AuNP concentrations of 5, 0.1 and 0.05 mg/L, and the suspension was characterized by UV-Vis. The concentration of AuNPs in suspension was determined using the LSPR peaks. This was only possible for the samples with
5 mg/L of AuNPs because the spectra for the other two concentrations (0.05 and 0.1 mg/L) were too weak and overlapped with the Na-montmorillonite spectra.

The spectra for the suspension of Na-montmorillonite and 5 mg/L of AuNPs (AuNP10, AuNP50 and, AuNP100) is shown in Figures 4.6 - 4.8. The samples were analyzed immediately after AuNPs were added and mixed, after 24 hours of mixing, and after centrifuging. All of the spectra were compared to the spectra of the suspension of Na-montmorillonite only, and the suspension of AuNPs only, and the simulated spectra of the mixture of Na-montmorillonite and AuNPs obtained by superimposing the two. Assuming that AuNPs associated with montmorillonite particles sediment after centrifugation, the AuNPs concentration obtained from the UV-Vis spectra of the centrifuged sample was subtracted from the initial concentration to determine the amount of AuNPs associated with Na-montmorillonite.

The spectrum for the freshly prepared mixture of AuNP10 with Na-montmorillonite showed a peak at ~ 520 nm from AuNP10 and a shoulder at ~ 243 nm from Na-montmorillonite (Figure 4.6, top). The spectrum obtained from the mixture of AuNP10 and Na-montmorillonite was in good agreement with the simulated spectrum in the visible region. However, it showed a shoulder at ~ 243 nm instead of a peak estimated from the simulation.

After 24 hours of mixing, the spectrum of the mixture also showed a peak at ~ 520 nm and another peak at ~ 243 nm from AuNP10 and Na-montmorillonite, respectively (Figure 4.6, top). What was a shoulder immediately after adding AuNP10 at ~ 243 nm formed a small peak, and the peak at ~ 520 nm became lower. The wavelength of the peaks was similar to the simulated spectrum; however, the shape of the peaks was different, and the intensities were lower than the simulated spectrum at both of the wavelengths.

After centrifuging the sample, the spectrum showed a shallow hump at ~ 520 nm and a small peak at ~ 266 nm (Figure 4.6, bottom). Significant changes were observed after centrifugation: overall intensity was decreased, the peak at ~ 243 nm disappeared and a small peak at ~266 nm appeared similar to the changes in the spectrum after centrifuging Na-montmorillonite suspension, and the peak ~ 520 nm considerably declined. The spectrum of the centrifuged sample was significantly different from the simulated spectrum, although the wavelengths of the peaks were approximately the same. The spectrum of the centrifuged sample was closer to
the spectrum of centrifuged Na-montmorillonite suspension, suggesting decreased contribution of AuNP10. From the peak height at ~ 520 nm, the amount of AuNP10 sorbed onto Na-montmorillonite was estimated to be 59 %.
Figure 4.6. UV-Vis Spectra for AuNP10 and Na-montmorillonite System

UV-Vis spectra for the suspension of AuNP10 and Na-montmorillonite: freshly mixed (top), 24 h mixing (middle), and centrifuged after 24 h mixing (bottom).
The spectrum obtained immediately after mixing AuNP50 to the suspension of Na-montmorillonite showed a peak at ~ 530 nm attributed to the AuNP50 LSPR band, and a shoulder at ~ 243 nm attributable to the Na-montmorillonite (Figure 4.7, top). The experimentally obtained spectrum for the AuNP50 and Na-montmorillonite system was in relatively good agreement with the simulated spectrum. It was overall slightly lower. Compared to the spectrum AuNP10, the shoulder at ~ 243 nm was more prominent.

After 24 hours of mixing, the spectrum of the mixture showed a small hump ~ 530 nm and another shoulder at ~ 263 nm. (Figure 4.7, middle). The shoulder observed immediately after mixing AuNP50 at ~ 243 nm disappeared, and a shoulder at ~ 263 nm appeared. The peak at ~ 530 nm significantly decreased. Compared to the simulated spectrum, the peak at ~ 530 nm was significantly lower, and the shoulder at ~ 263 nm was at different position compared to ~ 243 nm of the simulated spectrum.

After centrifuging the sample, the spectrum showed a very shallow hump at ~ 530 nm and a small peak at ~ 266 nm (Figure 4.7, bottom). The spectrum was almost the same as the spectrum of the centrifuged Na-montmorillonite suspension with almost no contribution of AuNP50. The amount of AuNP50 sorbed onto Na-montmorillonite was estimated to be 49 %.
Figure 4.7. UV-Vis Spectra for AuNP50 and Na-montmorillonite System

UV-Vis spectra for the suspension of AuNP50 and Na-montmorillonite: freshly mixed (top), 24 h mixing (middle), and centrifugated after 24 h mixing (bottom).
The absorption spectrum obtained for the freshly prepared mixture of AuNP100 and Na-montmorillonite shows a peak at ~ 565 nm, attributed to the AuNP100 LSPR band, and a shoulder at ~ 243 nm, attributed to the Na-montmorillonite (Figure 4.8, top). It was in relatively good agreement with the simulated spectrum. The deviation was at the wavelength shorter than ~ 300 nm, and the absorbance of the experimentally obtained spectrum was lower.

After 24 hours of mixing, the spectrum of the mixture showed a small hump at ~ 565 nm and another shoulder at ~ 266 nm (Figure 4.8, middle). The shoulder observed immediately after mixing AuNP100 at ~ 243 nm disappeared, and a shoulder at ~ 266 nm appeared. The peak at ~ 565 nm significantly decreased. These changes during the 24 hours of mixing were similar to AuNP50. Compared to the simulated spectrum, the peak at ~ 565 nm was much lower, and the shoulder at ~ 266 nm was at a different position.

The absorption spectrum after centrifugation showed a minimal absorption shoulder at ~ 565 nm and a small peak at ~ 266 nm (Figure 4.8, bottom). Centrifugation decreased the peak at ~ 565 nm to almost non-existent, and the peak at ~ 266 nm became lower as well. It was significantly different from the simulated spectrum. The amount of AuNP100 sorbed onto Na-montmorillonite was estimated to be 79 %.
Figure 4.8. UV-Vis Spectra for AuNP100 and Na-montmorillonite System

UV-Vis spectra for the suspension of AuNP100 and Na-montmorillonite: freshly mixed (top), 24 h mixing (middle), and centrifugated after 24 h mixing (bottom).
4.3.3 SEM Analysis of AuNPs and Na-montmorillonite Systems

SEM micrographs were obtained to study the Na-montmorillonite particles after the batch experiments with AuNP10, AuNP50 and AuNP100 (Figures 4.9 - 4.14). Deposition behavior was evaluated by examining the effect of different AuNP concentrations and washing to remove of the excess and weakly associated AuNPs. The AuNPs were easier to observe in the samples because of their characteristic brightness arising from the heavier elemental composition than the silicates and other components of the Na-montmorillonite sheets.

The observation of the AuNP10 particles after interacting with the Na-montmorillonite are shown in Figures 4.9 and 4.10. From the images, it can be observed that AuNP10 particles were near the clay edges however they were easily detected dispersed free and deposited randomly on top or under the Na-montmorillonite sheets at the different concentrations.

Minimal or very small amounts were possible to observe at the lower concentrations and no significant differences in the attachment behavior were detected between the samples prepared with and without washing (Figures 4.9 and 4.10).
Figure 4.9. SEM Image for AuNP10 Interactions with Na-montmorillonite Washed
The AuNP50 particles were found on clay edges but generally dispersed (i.e., settled from solution) in a way similar to AuNP10, although small amounts of AuNP50 particles were possible to detect at 0.05 and 0.1 mg/L Au-concentrations it was more significant at 5 mg/L as shown in Figures 4.11 and 4.12. Similarly, as for AuNP10, no significant differences in the deposition behavior was detected between the samples with and without washing.
Figure 4.11. SEM Image for AuNP50 Interactions with Na-montmorillonite Washed
The particles of AuNP100 were also found very little at Au-concentrations of 0.05 and 0.1 mg/L and more amounts at 5 mg/L as seen in Figures 4.13 and 4.14. The AuNP100 particles were found near clay edges and dispersed (i.e., settled from solution) and deposited similarly as AuNP10 and AuNP50. As was observed for AuNP10 and AuNP50, no significant differences in the attachments was detected between the samples with and without washing.
Figure 4.13. SEM Image for AuNP100 Interactions with Na-montmorillonite Washed
The AuNPs observed in the micrographs were confirmed by EDS where the AuNPs were confirmed since additional Au peaks were observed compared to the EDS spectrum of the Na-montmorillonite only samples.
4.4 Discussion

4.4.1 Interactions in AuNPs and Na-montmorillonite Systems

The microstructure observed for the Na-montmorillonite particles showed the characteristic thin edged (~ 1 nm) lamella shaped particles with sizes characteristic to clay minerals as seen in Figure 4.2 consistent with reported values [33] and indicate that there will be a predominance of larger flat surfaces with negative surface charges [26] due to the main component Si [28] although significant Al is present (Table 4.1, Figures 4.3 and 4.4), meaning that it didn't have influence on the surface charge.

The original AuNPs solutions show intense absorption in the visible light spectrum due to their LSPR (Figure 2.4) and in this region the UV-Vis spectra for Na-montmorillonite does not show an absorption peak, however it showed a strong absorption peak in the UV-Vis spectrum at around ~ 243 nm as shown in Figure 4.5, usually observed for clay minerals since they show absorbance in the far UV-Vis region [30] attributed to the presence of small amounts of iron (Fe³⁺) ions found coordinated with the octahedral alumina layer of each platelet [32-33] which is consistent with the small Fe present in the Na-montmorillonite used (Figures 4.3 - 4.4 and Table 4.2).

Changes in UV-Vis spectra can indicate attractive interactions between particles (i.e., aggregation) [23], thus the absorption spectra obtained for the AuNPs and Na-montmorillonite interactions from batch experiments were studied by UV-Vis spectroscopy respectively for AuNP10, AuNP50 and AuNP100 are shown in Figures 4.6, 4.7 and 4.8. The absorption spectra of the freshly prepared AuNPs and Na-montmorillonite systems (Figures 4.6, 4.7 and 4.8) showed two absorption maxima bands in relatively good agreement with the simulation spectra where the observed increase in the height of the AuNPs UV-Vis peaks are likely a consequence of the presence of the Na-montmorillonite particles scattering light thus increasing the absorption [34], however, after mixing for 24 hours, the AuNPs and Na-montmorillonite UV-Vis systems spectra (Figures 4.6 -4.8) showed changes in shape and intensity, where the intense peaks located in the visible region of the respective AuNPs became small humps of lower absorbance especially for AuNP50 and AuNP100 (Figures 4.7 and 4.8). Furthermore, the Na-montmorillonite peaks also showed changes where the shape became shoulder-like and it shifted to higher wavelengths for AuNP50 and AuNP100. The simulated UV-Vis addition
spectra showed overall inconsistency for the AuNPs in the visible region however the differences were more significant for AuNP50 and AuNP100.

It is possible that the alterations produced in the AuNPs and Na-montmorillonite systems (Figures 4.6 – 4.8) are a consequence of interactions occurring between them, since it is known that the absorption spectra for AuNPs such as peak decrease, band broadening and spectral LSPR peak shifting are indicators of aggregation and of its extent for nanoparticles including AgNPs [34] and AuNPs [23] as the used in the experiments.

The samples mixed for 24 hours were centrifuged to separate the excess AuNPs from the Na-montmorillonite and the supernatant UV-Vis was analyzed for Au-concentration for the samples of 5 mg/L (Figures 4.6 - 4.8) since the other concentrations were not possible to evaluate by UV-Vis. The absorption spectra obtained for the three centrifuged AuNPs samples showed a spectrum very similar to the UV-Vis spectra of the samples of pure Na-montmorillonite (without AuNPs) where the respective LSPR peaks of each AuNPs almost disappeared, especially for AuNP100. The amounts of AuNPs estimated to have attached to the Na-montmorillonite were 59, 49 and 79 % for AuNP10, AuNP50 and AuNP100, respectively. These values may be overestimating the attachment to clay since representative centrifugation (5 min at 12,000 g) of 5 mg/L solutions of AuNP50 and AuNP100 showed removal from the solution of 3 and 88% respectively, however effects of excess AuNPs were minimized during sample mounting for SEM observations.

To understand the AuNPs and Na-montmorillonite interactions suggested by the changes in the UV-Vis spectra, the deposition and distribution behavior of the AuNPs with Na-bentonite was investigated by SEM observations and the micrographs are shown in Figures 4.9 - 4.14 for AuNP10, AuNP50 and AuNP100, respectively. From the SEM images it can be seen that overall the AuNPs were found dispersed, as part of the solution and without a preferential deposition site or behavior.

The UV-Vis spectral feature changes can be a consequence of combined AuNPs and Na-montmorillonite surface interactions [34-36], where interactions were small with the edge faces as the SEM studies showed, inconsistent with a study using bare/uncoated AuNPs that were removed from the supernatants mostly due to their attachment at the edges of the clay particles.
under similar experimental pH conditions (low pH) attributed to the development of positive charges in the edges surfaces [7].

At the experimental conditions used (low IS and pH ~ 3), Na-montmorillonite particles will have overall negative zeta-potential of (Table 4.2) [29] since the surface or basal plane electrical double layer (EDL) is considered to be dominant, spilling over the thin edges (size order of about 1 nm) of the Na-montmorillonite particles, producing essentially negative zeta-potentials at most of the whole pH range [32]. However, the small mineral fractions (surface charge heterogeneities) of the edge surfaces of the Na-montmorillonite particles will develop local positive or less negatively surface charges (ζ-potentials) compared to the face surfaces or basal planes of Na-montmorillonite particles [32, 37]. This can occur since in the 2:1 sheet-like structure of montmorillonite, a layer of Al-octahedra lies between two layers of Si-tetrahedra, where the negative charges develop on the surface or basal plane while on the edges of the platelets charge heterogeneities (i.e., positive charges) can develop [14, 38].

As was reported for bare silver or gold nanoparticles [14, 22], attractive interactions between the AuNPs are probably influenced by the presence of positive (or less negative) surface charges (i.e., Al₂O₃) developed on the edges of the Na-montmorillonite particles. AuNPs deposition onto clay surfaces should be minimal as the DLVO theory predicts that electrostatic repulsive interactions are expected due to the similarities in surface charges (Table 2.1 and Table 4.2) as previous reports with bare nanoparticles showed [25].

The results from the SEM observations and EDS analyses for the batch experiments at pH 3 indicated that although the presence positive or less negative charges existed on the edge surfaces of the Na-montmorillonite particles since the PZC of the edges of clay materials vary in the pH range of 5 - 8 [29], the AuNPs removal from the supernatant solutions (~ 49 to 79 %) occurred on edges of clay particles however it was not mainly due to a preferential attachment onto them, contradicting the local DLVO theory which has successfully described platelet interactions in montmorillonite systems similar to the used in the current experiments [23].
4.4.2 DLVO Interaction Energies Between AuNPs and Na-Montmorillonite Particles

To better understand the AuNPs interactions with the Na-montmorillonite particles, the DLVO interaction energies were estimated and are presented in Figures 4.12 and 4.13 for the following possible interactions: 1) between the AuNPs and the Na-montmorillonite surfaces and 2) between the AuNPs and the Na-montmorillonite edge surfaces. The basic structure of montmorillonite is chemically composed of two Si-based tetrahedral sheets and one Al-based octahedral sheet “sandwiched” between the two tetrahedral sheets [32], thus the DLVO calculations should consider these physicochemical differences between the surface and the edges (i.e., surface charge and size).

The DLVO theory was developed to describe the interactions between two interacting surfaces and it is described as the total interaction energy \( U^{DLVO} \), which is estimated as the sum of the van der Waals \( U^{vdW} \) attractions and the double layer \( U^{EDL} \) repulsive energies [38-39], and can be expressed as Equation 4.1:

\[
U^{DLVO} = U^{vdW} + U^{EDL} \quad (4.1)
\]

where the \( U^{DLVO} \) is the total interaction energy between the different AuNPs through their PEG layers with the Na-montmorillonite particles surfaces (i.e., surfaces and edges) in a media (assumed DI water with low ionic strength ~ 0.001 M) with the data taken from Table 4.2.

Table 4.2 Na-montmorillonite Physicochemical Properties

<table>
<thead>
<tr>
<th>Na-montmorillonite Surface</th>
<th>( \zeta )-potential (mV)</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mont. Surface [^{[27]}]</td>
<td>-30</td>
<td>243</td>
</tr>
<tr>
<td>Na-Mont. Edge [^{[27]}]</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

The attractive \( U^{vdW} \) interactions occurring between the AuNPs and the surface of a particle of Na-montmorillonite were estimated considering them as sphere - plate interactions which can be calculated using the following equation [40]:
\[ U^{vdW} = -\left( \frac{A_{\text{Mont-Surface}}a_p}{6h} \right) \left( 1 + \frac{14h}{\lambda} \right)^{-1} \]  

(4.2)

where \( A_{\text{Mont-Surface}} \) is the Hamaker constant for the interacting surfaces (PEG and Na-montmorillonite surfaces in water); \( a_p \) is the AuNPs radius (considering \( d_{\text{DLS}} \)), \( h \) is the separating distance, and \( \lambda \) is the characteristic wavelength of the dielectric, considered to be usually 100 nm [41].

The Hamaker constants for the two interacting materials in a aqueous medium were calculated based on the Hamaker constants of the materials in a vacuum \( A_{\text{PEG}}, A_{\text{H}_2\text{O}} \) and the \( A_{\text{Mont-Surface}} \) values were estimated considering the Hamaker constants for the surfaces in a third media [42] and were calculated with the following equation [42]:

\[ A_{\text{Mont-Surface}} = A_{\text{PEG/H}_2\text{O/Surface}} = (A_{\text{PEG}}^{1/2} - A_{\text{H}_2\text{O}}^{1/2}) (A_{\text{Surface}}^{1/2} - A_{\text{H}_2\text{O}}^{1/2}) \]  

(4.3)

Based on reported Hamaker values in vacuo for \( A_{\text{H}_2\text{O}}, A_{\text{PEG}} \) and \( A_{\text{Surface}} \) [37, 42-43], the obtained Hamaker constant for the Na-montmorillonite particle surfaces (\( A_{\text{Mont-Surface}} \)) calculated with Equation (4.3) was found to be \( 4.89 \times 10^{-21} \) J.

The \( U^{\text{EDL}} \) calculations were done with Equation 4.4 by considering the interactions as between them as sphere - plane and it can be described by the following expression [44]:

\[ U^{\text{EDL}} = \pi \varepsilon_0 \varepsilon_r a_p \left[ 2\zeta_{\text{PEG}}\zeta_{\text{Mont}} \ln \left( \frac{1+e^{-\kappa h}}{1-e^{-\kappa h}} \right) + (\zeta_{\text{PEG}}^2 + \zeta_{\text{Mont}}^2) \ln(1 - e^{-2\kappa h}) \right] \]  

(4.4)

where \( U^{\text{EDL}} \) is the electrostatic repulsive interaction energy between the PEG coating of the AuNPs and the Na-montmorillonite particles surfaces in a water medium, \( \varepsilon_r \) is the relative permittivity of water (78.5), \( \varepsilon_0 \) is the permittivity of a vacuum (8.854 \( \times 10^{-12} \)), \( a_p \) is the AuNPs radius (considering \( d_{\text{DLS}} \)), \( \zeta_{\text{PEG}} \) and \( \zeta_{\text{Mont}} \) are the surface potentials of the interacting surfaces (AuNPs and Na-montmorillonite \( \zeta \)-potentials taken from Table 2.1 and Table 4.2 were used), \( h \) is the separation distance and \( \kappa \) is the inverse Debye screening length, defined as:

\[ \kappa = \sqrt{\frac{e^2 \Sigma Z_i^2}{\varepsilon_0 \varepsilon_r k_B T}} \]  

(4.5)
where \(e\) is the electron charge \((1.60 \times 10^{-19} \text{C})\), \(n_i\) and \(z_i\) are the concentration and valence of ion \(i\) and \(T\) corresponds to the temperature \((298 \text{ K})\).

The DLVO estimations for the interaction energies of the AuNPs with the edges of the Na-montmorillonite particles were performed with the following equation for the attractive \(U_{vdW}\) considering their interactions as between two spherical particles (AuNPs and Na-montmorillonite) of dissimilar sizes as follows [45]:

\[
U_{vdW} = - \frac{A_{\text{Mont-Edge}}a_{p1}a_{p2}}{a_{p1} + a_{p2}} \quad (4.6)
\]

where \(A_{\text{Mont-Edge}}\) is the Hamaker constant for the interacting surfaces (PEG and Na-montmorillonite surfaces in water), \(a_{p1}\) is the is the AuNPs radius (considering \(d_{\text{DLS}}\)) from Table 2.1 and \(a_{p2}\) is the Na-montmorillonite particle radius obtained from previous reported values that are similar to the observed sizes (Figure 4.2) [32].

\(A_{\text{Mont-Edge}}\) Hamaker constants between the two interacting materials in an aqueous medium were calculated based on the Hamaker constants of the materials in a vacuum \(A_{\text{PEG}}, A_{\text{H2O}}\) and the \(A_{\text{Mont-Edge}}\) values were calculated with Equation (4.3).

Using reported Hamaker values in vacuo for \(A_{\text{H2O}}, A_{\text{PEG}}\) and \(A_{\text{Edge}}\) [37, 42-43], the Hamaker constant for the Na-montmorillonite particles edges \((A_{\text{Mont-Edge}})\) calculated with Equation 4.3 was found to be \(4.59 \times 10^{-21} \text{ J}\).

The repulsive electrostatic \(U_{EDL}\) were calculated considering the interactions as between two dissimilar sized spheres, where the following equation was used [46]:

\[
U_{EDL} = 64\pi\varepsilon_0\varepsilon_rY_1Y_2\frac{a_{p1}a_{p2}}{(a_{p1} + a_{p2})}(\frac{k_BT}{z\varepsilon})^2\exp\left(-\kappa D\right) \quad (4.7)
\]

where in \(z\) is the ion valence and \(\gamma_i\) is defined as:

\[
\gamma_i = \tanh\left(\frac{z\varepsilon \psi_i}{4k_BT}\right) \quad (4.8)
\]
where $\psi_i$ are the surface potentials of the two particles, approximated as the zeta-potentials from Table 2.1 and Table 4.2.

The total interaction energies ($U^{DLVO}$) calculated for the different AuNPs with the different Na-montmorillonite surfaces can be plotted against the separation distance ($h$) in nm and they are shown in Figures 4.15 and 4.16. The graphs show the AuNPs interactions with the surfaces (Figure 4.15) and with the edges (Figure 4.16) of the Na-montmorillonite particles, where the plots vertical axis is shown in $k_B T$ terms, were $k_B$ is the Boltzmann constant and $T$ is absolute temperature.

The total DLVO interactions between the AuNPs and the Na-montmorillonite surfaces in Figure 4.15 show high energy barriers for all the AuNPs. The height of the energy barriers (against surface interactions) were found to be of ~ 6, 54 and 63 $k_B T$ for AuNP10, AuNP50 and AuNP100, respectively and their maximum heights were located at short separation distances (between 1 – 5 nm) between the interacting surfaces.

![Figure 4.15. DLVO Plot for AuNPs and Na-montmorillonite Surface Interactions](image)

The obtained DLVO energy profiles (Figures 4.15) show the characteristic attractive deep primary wells at smaller distances ($h$) which are considered to be responsible for irreversible attachment, at increased separation distances the maximum energy barriers are observed with their values shown in Table 4.3 and minimal shallow secondary minima or secondary energy...
wells at larger distances, considered to produce reversible (weak) attractive interactions since they are extremely shallow compared to the primary energy wells.

**Table 4.3 Calculated Maximum Energy Barriers ($U_{DLVO}$) and Distances for AuNPs and Na-montmorillonite Surfaces/Edge interactions**

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Surface Interactions Primary Energy Barrier</th>
<th>Distance $h$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$U_{DLVO}$ $(k_BT)$</td>
<td>(nm)</td>
</tr>
<tr>
<td>AuNP10</td>
<td>6.0</td>
<td>5</td>
</tr>
<tr>
<td>AuNP50</td>
<td>54.0</td>
<td>1</td>
</tr>
<tr>
<td>AuNP100</td>
<td>63.0</td>
<td>2</td>
</tr>
</tbody>
</table>

The total DLVO interactions between the AuNPs and the edge surfaces of Na-montmorillonite shown in Figure 4.16 did not show the presence of energy barriers (against edge interactions) for all the AuNPs and only deep wells at short distances were observed, meaning that attractive interactions should occur unhindered.

Since the Na-montmorillonite particles surfaces and the AuNPs are negatively charged (low IS and pH ~ 3) [47-50], the large energy barriers for the AuNPs and Na-montmorillonite surface interactions (Table 4.3) are a consequence of similarly charged surfaces interacting thus producing strong electrostatic repulsions, while the AuNPs and Na-montmorillonite edge interactions did not produce barriers as a consequence of oppositely charged (less oppositely charged) surfaces interacting thus producing reduced interactions (i.e., localized deposition) due to minimal or non-existing electrostatic repulsions thus eliminating primary energy barriers.
The SEM micrographs obtained (Figures 4.9 to 4.14) did not show that AuNPs did interact attractively (or deposited) preferably with the edge surface of the Na-montmorillonite particles, inconsistent with earlier studies [14, 23] and with the results from the DLVO energy calculations (Figure 4.15 and 4.16). Thus, it is possible that the AuNPs and Na-montmorillonite edges interactions were modified by factors not included in previous studies or the DLVO theory responsible for the observed discrepancies.

4.4.3 AuNPs Deposition Behavior Comparison with Silica Sand and Na-montmorillonite

The AuNPs interactions with silica sand particles produced attractive interactions inconsistent with the DLVO theory predictions (Figures 2.13 - 2.15) since column retention was observed (Figure 2.10) and UV-Vis (Figure 2.12) and SEM (Figures 3.12 and 3.13) analyses indicated that AuNPs aggregation occurred.

The surfaces of the silica sand particles have both physical and chemical heterogeneities on its surface as shown by SEM and EDS and in some cases together (Figure 3.6 and 3.7). Small amounts of AuNP10 were dispersed on the silica sand surfaces and increased deposition and aggregation was detected for AuNP50 and AuNP100 especially in rough areas. The EDS analyses of some of the areas with AuNPs showed that mineral fractions existed in these areas.
A distribution of secondary mineral abundance has been related to distribution of potentials in the surface of the silica sand where local attractive interactions are possible with the AuNPs including aggregation [51] and in some cases it can occur in combination with local flow disturbances as has been previously proposed [52].

In the case for Na-montmorillonite, DLVO attractive interactions with the AuNPs are considered unfavorable with the surfaces (similarly charged surfaces) but possible with the edges (Figures 4.15 and 4.16 respectively) due to opposing charges, however minimal attractions (enhanced deposition and/or aggregation) of the AuNPs with the surface charge heterogeneities on the Na-montmorillonite edges (produced at low pH) were observed.

Na-montmorillonite particles also have physical and chemical heterogeneities as were observed by TEM, SEM and EDS which are different than silica sand. Na-montmorillonite platelets have the charge heterogeneities localized in the nanometer thick (~ 1 nm) edges of their flat surfaces (Figure 4.2). This enclosed and small sized charge heterogeneities contrast with the larger areas with charge heterogeneities that can exist on the surfaces of silica sand (Figure 3.6 and 3.7). By their size scale, the clay edge charge heterogeneities can be acting as charge heterogeneities without the roughness found on silica sand particles, being able to produce small single-particle deposition as was observed by SEM (Figures 4.9 - 4.14).

The interaction behavior showed by the Na-montmorillonite particles with the AuNPs contradicts studies that showed near complete edge attachments using uncoated (bare) metal nanoparticles [14, 32]. The discrepancies of our findings between previous results using uncoated nanoparticles and with the DLVO theory are suggesting that effects not considered or existent in them are likely producing such discrepancies, and as was discussed for the experiments with silica sand, the steric stability introduced by the PEG coatings on the AuNPs considered to be the main stabilizing mechanism for the AuNPs over electrostatic stabilization (Figure 2.8) against superficial interactions can explain this deviation by reducing or eliminating possible attractive interactions.

It is still not possible to separate and measure independently the individual effects of surface morphology and chemical composition on the deposition of colloids since they are often closely related especially in natural solids found in aquifers [52], where particle surface
irregularities will exist and different accessory minerals will be found as coatings or as fillings in cavities or rough patches [52].

Furthermore, systems with media of increased complexity are to be expected since additionally a variety of organic material can also exist in the interstitial regions of the surfaces of natural soils [52]. Thus, improving the characterization methods and techniques of the interacting surfaces (colloids and media) will help improve the current understanding of colloidal interactions in order to produce reliable models that predict colloids fate and transport and related effects such as colloidal facilitated transport of radionuclides.

4.5 Conclusions

Due to its properties and characteristics, the disposal of HLW considers the use of clay material (such as sodium bentonite) as buffer material, one of the key elements in the engineered barrier systems developed for the long-term containment of radionuclides. Potential interactions between clay particles with other colloidal material (generated in-situ or naturally existing) in disturbed systems (i.e., due to bentonite erosion) cannot be avoided, thus understanding the possible interactions between them is of high importance for the safety assessment of geological repositories.

In this work we investigated the potential interactions between Na-montmorillonite particles surfaces with different concentrations of PEGylated AuNPs of different sizes under low IS and pH conditions where AuNPs attachment can occur due to the development of attractive charge heterogeneities in the edge surfaces of the Na-montmorillonite.

The experimental results showed that the AuNPs attachment onto the Na-montmorillonite edges was small contrary to the DLVO theoretical calculations and with previous studies using bare or uncoated metallic-core nanoparticles (i.e., AgNPs and AuNPs) that showed enhanced attachments to the edges. The discrepancies produced are possibly a consequence of a combined effect between a distribution of small charge heterogeneities (~ 1 nm) that were likely not strong or large enough to overcome the steric stabilization found on the AuNPs in order to produce and sustain significant deposition or aggregation and/or to the absence of surface roughness, but the evaluation of their contributions to the AuNPs deposition was not possible.
In contrast, the surface heterogeneities that exist on the surfaces of silica sand particles were in some cases effective and produced larger deposition and/or aggregation of larger AuNPs especially near rough areas.

The results indicate that attractive interactions produced by the surface charge heterogeneities developed on the clay edges were very important in enhancing the deposition of nanoparticles (i.e., AuNPs) without polymeric coatings, however if the nanoparticles are protected by a polymeric coating (i.e., PEG) as the AuNPs used herein, similar attractive interactions with the charge heterogeneities are likely too weak for the used PEG-coated AuNPs probably due to a reduced area effect or related to the available amount of secondary minerals where to attach.

These findings can be applied to underground environments related to deep geological repositories, where colloids generated or liberated form the repository materials such as from the bentonite used as buffer material can interact with other existing colloids or nanoparticles (i.e., NOM) in a similar behavior which was inconsistent with current theoretical predictions. Thus, for the safety assessment of HLW repositories consideration of the local physicochemical characteristics and differences of the surfaces involved are necessary in order to determine potential interactions that can alter colloidal fate and transport.
References


Chapter 5. Conclusions
Understanding the interaction behavior between colloidal particles with engineered and natural barrier system materials like the ones found in HLW deep geological disposal facilities is key to improve our ability to predict the system safety and reliability, and the results presented in this work can help to improve the current understanding of how the properties of the materials involved can impact in the way colloids and/or nanoparticles interact with silica sand porous media or with clay particles.

Batch deposition and column transport experiments were conducted using gold nanoparticles (AuNPs) of three different sizes in order to investigate the effects of colloidal properties on their migration behaviors. The two most important findings where: 1) that the deposition and aggregation were mainly observed for larger AuNPs in both the batch and the column experiments, despite the predictions from the DLVO theory that predicted that smaller nanoparticles were more likely to deposit and/or to aggregate, implying the importance of non-DLVO interactions and 2) that the occurrence of deposition despite unfavorable deposition conditions for the AuNPs onto silica sand may be a result of surface charge heterogeneities, where the sloping plateaus observed in the BTCs of AuNPs in the column experiments indicated that a limited number of sites exhibited attractive interactions with AuNPs.

One of the possible non-DLVO forces important in our experimental system are the steric effects imparted by the poly(ethylene glycol) (PEG) layer. The thinner PEG layer of the larger AuNPs may have been unable to maintain long enough separation distance for attractive interactions to result in deposition and aggregation, whereas the thicker PEG-layer of AuNP10 may have been able to stabilize them against deposition and aggregation.

Silica sand surfaces after deposition experiments with AuNPs were analyzed by SEM-EDS in order to elucidate the mechanisms for deposition and aggregation in relation to surface interactions/properties. Deposition of AuNPs onto silica sand surfaces occurred, but only in small areas, which was consistent with the predictions from DLVO theory that overall deposition is not expected due repulsive interactions between AuNPs and silica sand. All of the AuNPs of different sizes showed deposition but it was more significant for AuNP50 and AuNP100. Deposition of AuNP50 and AuNP100 occurred more near the rough surfaces of the silica sand. This may suggest that charge heterogeneity caused by the presence of secondary minerals in these areas may influence the deposition behavior, however another possibility are the physical effects and local hydrodynamic flow disturbances in these rough surfaces. From
the SEM-EDS observations, it was not possible to discuss and compare the significance of these two effects. Mechanisms for the deposition of AuNP10 may be different because AuNP10 was deposited dispersed on a smoother area of the silica sand.

Aggregation was also directly observed by SEM for AuNP50 and AuNP100, but minimal for AuNP10. Degree of aggregation was more significant for AuNP100 with more clusters observed than AuNP50 that showed more pairs and triplets, thus stronger interactions were suggested for larger AuNPs for both between the surfaces of AuNP and silica sand, and between AuNPs. These observations may suggest the significance of non-DLVO interactions such as steric effects.

Bentonite is one of the proposed buffer materials and consists mainly of platelet-shaped montmorillonite particles and is another type of subsurface material with physical and chemical surface heterogeneities that can develop charge heterogeneity on their surfaces, especially in their edges. The characteristics of montmorillonite clays produces properties such as strong sorption capacity useful for their application as buffer material in HLW repositories (i.e., Na-montmorillonite in Japan), making it one of the key elements in the engineered barrier systems developed for the long-term containment of radionuclides.

Potential interactions between clay particles with other colloidal material (generated in-situ or naturally existing) in disturbed systems (i.e., due to bentonite erosion) cannot be avoided, thus understanding the possible interactions between them is of high importance for the safety assessment of HLW geological repositories. Potential attractive interactions between Na-montmorillonite particles surfaces with colloidal particles as the AuNPs used herein can occur especially under low IS and/or pH conditions where attachment can occur due to the development of charge heterogeneities in the edge surfaces of the Na-montmorillonite particles.

The experimental results showed that the AuNPs attachment onto the Na-montmorillonite edges was small contrary to the DLVO theoretical calculations and with previous studies using bare or uncoated metallic-core nanoparticles (i.e., AgNPs and AuNPs) that showed enhanced attachments to the edges. The discrepancies produced are possibly a consequence of a combined effect between a distribution of small charge heterogeneities (~ 1 nm) that were likely not strong or large enough (i.e., to overcome the steric stabilization found on the AuNPs) in order to produce and sustain significant AuNPs deposition and/or aggregation and/or to the
absence of surface roughness, however it remains unclear how they contribute to the deposition or aggregation. In contrast, the surface heterogeneities that exist on the surfaces of the silica sand particles were in some cases sufficient to produce larger AuNPs deposition and/or aggregation near rough areas.

The results indicate that the attractive interactions produced by the surface charge heterogeneities developed on the clay edges were very important in enhancing the deposition of nanoparticles (i.e., AuNPs) without polymeric coatings, however if the nanoparticles are protected by a polymeric coating (i.e., PEG) as the AuNPs used herein, the same attractive interactions of the AuNPs with the charge heterogeneities are likely not strong enough probably due to a reduced area effect or related to the available amount of secondary minerals where to attach.

These findings can be applied to underground environments related to deep geological repositories, where existing colloids or nanoparticles may attach to natural organic matter (NOM) and modify their migration behavior with natural barriers (silica sand) or with engineered barrier materials (Na-montmorillonite) in way not consisting with theoretical models or with experiments using uncoated (bare) nanoparticles.

Further studies on non-DLVO forces including steric effects and consideration of the local physicochemical characteristics and differences of the surfaces involved are necessary to fully understand and to incorporate the interactions in the modelling of colloidal transport necessary for the performance assessment of HLW disposal facilities.
Research Achievements

Oral Presentations

- Atomic Energy Society of Japan (AESJ), Hokkaido Chapter Meeting
  Sapporo, Japan, February 2018.

- Atomic Energy Society of Japan (AESJ) Annual Meeting
  Osaka, Japan, March 2018.

- Atomic Energy Society of Japan (AESJ) Fall Meeting
  Okayama, Japan, September 2018.

- Atomic Energy Society of Japan (AESJ) Fall Meeting
  Sapporo, Japan, September 2017.

Poster Presentations

- Atomic Energy Society of Japan (AESJ) 34th Backend Section Seminar.
  Sendai, Japan, August 2018.

Research Awards

- Student Excellence Lecture Award
  Atomic Energy Society of Japan (AESJ) Fall Meeting.
  Okayama, Japan, September 2018.

- Encouragement Award,
  Atomic Energy Society of Japan (AESJ), Hokkaido Branch Meeting.
  Sapporo, February 2018.
Appendix A. AuNP10 Deposition on silica sand

Figure 1. Deposition of AuNP10 on silica sand.

Figure 2. Deposition of AuNP10 on silica sand.
Figure 3. Deposition of AuNP10 on silica sand.

Figure 4. Deposition of AuNP10 on silica sand.
Figure 5. Deposition of AuNP10 on silica sand.

Figure 6. Deposition of AuNP10 on silica sand.
Figure 7. Deposition of AuNP10 on silica sand.

Figure 8. Deposition of AuNP10 on silica sand.
Figure 9. Deposition of AuNP10 on silica sand.

Figure 10. Deposition of AuNP10 on silica sand.
Figure 11. Deposition of AuNP10 on silica sand.

Figure 12. Deposition of AuNP10 on silica sand.
Figure 13. Deposition of AuNP10 on silica sand.

Figure 14. Deposition of AuNP10 on silica sand.
Figure 15. Deposition of AuNP10 on silica sand.

Figure 16. Deposition of AuNP10 on silica sand.
Figure 17. Deposition of AuNP10 on silica sand.

Figure 18. Deposition of AuNP10 on silica sand.
Figure 19. Deposition of AuNP10 on silica sand.

Figure 20. Deposition of AuNP10 on silica sand.
Figure 21. Deposition of AuNP10 on silica sand.

Figure 22. Deposition of AuNP10 on silica sand.
Figure 23. Deposition of AuNP10 on silica sand.

Figure 24. Deposition of AuNP10 on silica sand.
Figure 25. Deposition of AuNP10 on silica sand.

Figure 26. Deposition of AuNP10 on silica sand.
Figure 27. Deposition of AuNP10 on silica sand.
Appendix B. AuNP50 Deposition on silica sand

Figure 1. Deposition of AuNP50 on silica sand.

Figure 2. Deposition of AuNP50 on silica sand.
Figure 3. Deposition of AuNP50 on silica sand.

Figure 4. Deposition of AuNP50 on silica sand.
Figure 5. Deposition of AuNP50 on silica sand.

Figure 6. Deposition of AuNP50 on silica sand.
Figure 7. Deposition of AuNP50 on silica sand.

Figure 8. Deposition of AuNP50 on silica sand.
Figure 9. Deposition of AuNP50 on silica sand.

Figure 10. Deposition of AuNP50 on silica sand.
Figure 11. Deposition of AuNP50 on silica sand.

Figure 12. Deposition of AuNP50 on silica sand.
Figure 13. Deposition of AuNP50 on silica sand.

Figure 14. Deposition of AuNP50 on silica sand.
Figure 15. Deposition of AuNP50 on silica sand.

Figure 16. Deposition of AuNP50 on silica sand.
Figure 17. Deposition of AuNP50 on silica sand.

Figure 18. Deposition of AuNP50 on silica sand.
Figure 19. Deposition of AuNP50 on silica sand.

Figure 20. Deposition of AuNP50 on silica sand.
Appendix C. AuNP100 Deposition on silica sand

Figure 1. Deposition of AuNP100 on silica sand.

Figure 2. Deposition of AuNP100 on silica sand.
Figure 3. Deposition of AuNP100 on silica sand.

Figure 4. Deposition of AuNP100 on silica sand.
Figure 5. Deposition of AuNP100 on silica sand.

Figure 6. Deposition of AuNP100 on silica sand.
Figure 7. Deposition of AuNP100 on silica sand.

Figure 8. Deposition of AuNP100 on silica sand.
Figure 9. Deposition of AuNP100 on silica sand.

Figure 10. Deposition of AuNP100 on silica sand.
Figure 11. Deposition of AuNP100 on silica sand.

Figure 12. Deposition of AuNP100 on silica sand.
Figure 13. Deposition of AuNP100 on silica sand.

Figure 14. Deposition of AuNP100 on silica sand.
Figure 15. Deposition of AuNP100 on silica sand.

Figure 16. Deposition of AuNP100 on silica sand.
Figure 17. Deposition of AuNP100 on silica sand.

Figure 18. Deposition of AuNP100 on silica sand.
Figure 19. Deposition of AuNP100 on silica sand.

Figure 20. Deposition of AuNP100 on silica sand.