Impact of gravity, collector surface roughness and fracture orientation on colloid retention kinetics in an artificial fracture

M. Stoll [a,*], F.M. Huber [a], G.K. Darbha [a,b], E. Schill [a], T. Schäfer [a,c]

[a] Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany
[b] National Institute of Technology, Tadepalligudem, Andhra Pradesh, 534101, India
[c] Karlsruhe Institute of Technology (KIT), Institute of Applied Geosciences (AGW), Environmental Geology, Karlsruhe, Germany

GRAPHICAL ABSTRACT
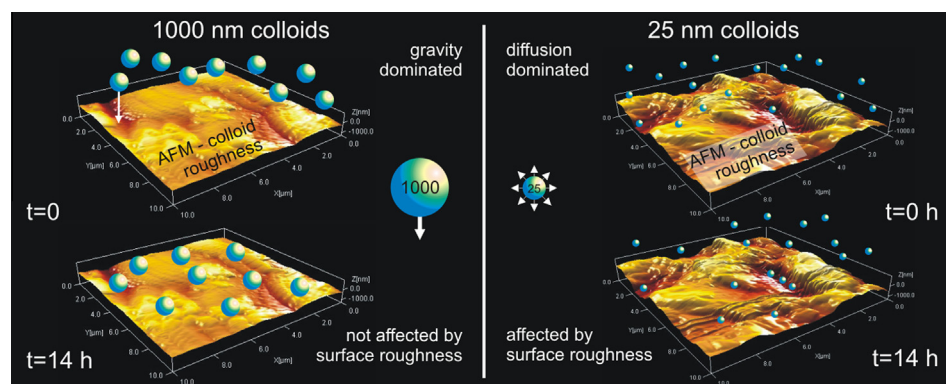
ARTICLE INFO

ABSTRACT

The interaction of monodisperse fluorescent carboxylated polystyrene colloids (25 nm and 1000 nm diameter) with a cut granodiorite surface (Grimsel granodiorite; Switzerland) and with acrylic glass is investigated both experimentally and numerically. Colloid transport experiments are conducted in a parallel plate type fracture flow cell with an aperture of 0.75 mm at pH 5 under low ionic strength (1 mM NaCl) and under laminar flow (7 mL/h) conditions. The study focuses on the effect of residence time, colloid size, collector material and fracture orientation on colloid retention. Long colloid residence times are achieved by stop-flow experiments. Using atomic force microscopy and, more specifically, the colloid probe technique surface roughness and force distance information of the collector material (granodiorite or acrylic glass) as a function of probe size (cantilever) are obtained. The experiments are modeled using COMSOL Multiphysics® (2-D numerical simulations). The experimental and the modeled results lead to the conclusion that large colloids (1000 nm diameter) undergo sedimentation and deposition on the surface during stop-flow. Collector interaction is not affected by the surface roughness variation. Contrariwise, for the investigated 25 nm colloids sedimentation does not play a role under the experimental conditions and collector interaction is triggered by surface inhomogeneities such as surface roughness.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Colloids such as clay minerals and humic substances are ubiquitous in surface and subsurface waters. Because of the low settling

* Corresponding author.
    E-mail address: madeleine.stoll@kit.edu (M. Stoll).

velocity, small colloids ($\leqslant 1\ \mu m$) can travel long distances, e.g. through fractures or porous media [1,2]. Colloid transport in geological formations has been studied for decades. For example, there are environmental issues such as contaminant transport in groundwater [3–7] and more specifically colloid facilitated radionuclide transport *inter alia* at the Nevada Test Site and in the Underground Research Laboratory (URL) experiments at the Grimsel Test Site [8–11]. Besides negative economic issues such as pore clogging (formation damage) during extraction of fluids from the subsurface [e.g. 12,13], in fractured reservoirs, deposition of clay colloids enhances reactivation potential and thus, permeability [14,15]. In this study we focus on fractured media. Fractures serve as preferential conduits for colloids. This is due to (i) large flow diameters that enable high flow velocities compared to the surrounding matrix, (ii) mostly unfavorable conditions for attachment due to negatively charged surfaces of colloids and fractured walls and (iii) negligible matrix diffusion of colloids in contrast to solutes [2,3,16,17]. The mechanistic understanding of colloid transport determining processes in fractured rocks is a key to make reliable long-term predictions on the fate of hazardous elements attached to colloids. Major processes acting on colloids during the transport in saturated fractures are advection, dispersion, adsorption, desorption and physical straining [18]. Colloids are transported through conductive fractures by advection. Under high groundwater flow conditions it has been shown that the mean colloid transport velocity is enhanced in contrast to solute conservative tracers [10,11,16,19–27]. This can be explained by a combination of three effects: size exclusion, charge exclusion and Taylor dispersion [21,25]. Thus, colloids migrate through a comparably smaller effective volume and due to their small diffusivity the colloids diffuse too slowly to enter low or stagnant flow zones [19]. According to the Stokes-Einstein equation [28] this effect increases with increasing colloid size because of a colloid radius dependent lower diffusion coefficient. James and Chrysikopoulos [29] showed that colloids follow the highest flow velocities in the center of the fracture. Thus, colloids follow a parabolic velocity profile and travel midstream while migrating through a fracture.

Beside the fraction that is transported unretarded, colloid retention occurs to a certain extent. The main mechanisms for retention are physical straining, sedimentation, (matrix) diffusion, and adsorption/desorption [18]. Colloid deposition on solid surfaces is subdivided into two processes: transport and attachment [30]. The transport process can be described by advection-diffusion equations and it depicts the movement of the colloids from the bulk fluid to the vicinity of the fracture surface. The attachment process depends on the interaction forces between the colloids and the collector surface (e.g. fracture wall) discriminating between electrostatically favorable and unfavorable conditions of attachment [31]. This electrostatic dependent interaction is often described by the DLVO-Theory (for further information see e.g. van Oss et al. [32]). However, both field- and laboratory experiments found significant colloid retention even under electrostatically unfavorable conditions, where repulsive forces dominate [33–35]. For example, Albarran et al. [36] analyzed the transport behavior of artificial (gold and latex) and natural (smectite) colloids in colloid transport experiments through a rough granite fracture under unfavorable attachment conditions. They observed colloid retention for all colloid types and sizes. They concluded that this retention is not driven by the chemical composition of the minerals but rather by mineral porosity, surface roughness, crystal defects, grain boundaries or small scale chemical and/or charge heterogeneities. This conclusion was made in several comparable studies as well [e.g. 31,37–39]. On a bigger scale, in colloid transport experiments through a natural fractured granite block ($83 \times 90 \times 60$ cm), Vilks and Bachinski [40] investigated the influence of colloid size, velocity, flow direction and flow path on

colloid retention. They showed that the transport of colloids is highly sensitive to variations in flow path and flow direction.

In studies on low density carboxylated polystyrene spheres Cumbie and McKay [41] discovered a significant influence of colloid diameter on transport and retention in fractured shale saprolite. The optimum transported colloid size was found to be 500 nm. In accordance with filtration theory [42,43], both smaller (50–100 nm diameter) and bigger colloids (1000 nm diameter) showed higher filtration factors and therefore lower recovery – the smaller colloids due to diffusion and the bigger colloids due to sedimentation. This conclusion verifies the experimental results and conceptual model of Reimus [19]. The influence of collector surface orientation on colloid deposition was investigated in detail by Dokou et al. [44] by means of static batch experiments using colloids of different sizes and densities and vertical or horizontal coated glass surfaces. They found that under stagnant conditions gravity is negligible for low density colloids ($1.05\ g/cm^3$) with sizes $< 1\ \mu m$. In experiments using bigger or denser colloids ($2.07\ g/cm^3$ or $19.20\ g/cm^3$) they observed a higher amount of colloids on horizontal glass samples than on vertical glass samples. The impact of gravity on transported colloids was shown in numerical studies of James and Chrysikopoulos [45] who investigated the influence of fracture orientation on colloid transport through a single fracture.

In all these studies mentioned above, the influence of collector roughness on colloid retention as a function of colloid size was not investigated in detail. Therefore, the aim of this study is to gain process understanding of colloid size dependent transport and deposition on cut granodiorite surfaces by a combination of the following methodical approaches:

(i) Macro-scale colloid transport experiments under laminar flow conditions (7 mL/h) using a parallel plate type fracture flow cell and a background electrolyte of 1 mM NaCl at pH 5 establishing bulk unfavorable colloid attachment conditions.

(ii) Micro- to nano-scale investigations on the colloid–collector interaction by means of atomic force microscopy (AFM) characterizing (a) the collector surface roughness and (b) the interaction forces using the colloid probe technique.

(iii) The experiments are accompanied by 2-D numerical simulations using COMSOL Multiphysics®. The laminar flow and the colloid transport are solved using the Navier-Stokes equation and a Lagrangian particle tracing approach. Implemented forces which are acting on the colloids are gravity, drag force and Brownian motion.

Parameter variations in the macro-scale experiments included (a) the flow velocity with flow interruptions ("stop-flow") to simulate long residence times, (b) the collector surface roughness in comparison to acrylic glass as reference material, (c) the fracture orientation to sound the potential influence of gravity and (d) the colloid size by using 25 nm and 1000 nm polystyrene carboxylated spheres.

2. Material and methods

2.1. Artificial fracture flow cell

A parallel plate type fracture flow cell made of acrylic glass (Polymethyl methacrylate, PMMA, trademark Plexiglas®) has been designed and constructed. The scheme in Fig. 1a shows the fracture cell dimensions and design. The main parts consist of two cylindrical bodies: one larger body with an inlet and an outlet and one disc like body. A cavity with the dimensions of 38.3 mm diameter and 0.75 mm depth has been drilled into the bottom side of the larger upper body. After assembling the flow cell, the cavity represents the artificial fracture aperture with the top side surface always