Colloids and Surfaces A 529 (2017) 222–230

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Parallel-plate fracture transport experiments of nanoparticulate illite in the ultra-trace concentration range investigated by Laser-Induced Breakdown Detection (LIBD)

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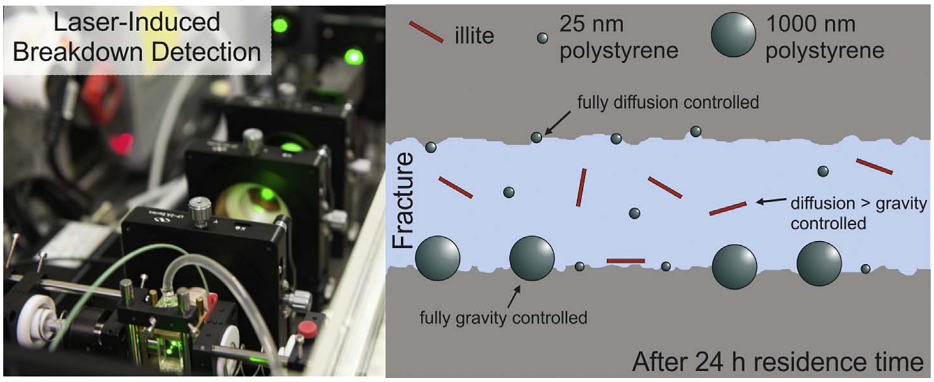
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Illite
Polydispersity
Laser-induced breakdown detection
Fracture
Colloid transport
Carboxylated polystyrene spheres

ABSTRACT

This study investigates the appropriateness of monodisperse carboxylated polystyrene spheres as clay colloid analogues. Colloid transport experiments using Na-illite are conducted within a parallel-plate fracture flow cell with an aperture of 0.75 mm at pH 5 under low ionic strength (1 mM NaCl) and laminar flow (7 mL/h) conditions. The effects of collector surface material (Grimsel granodiorite or acrylic glass), fracture orientation and residence time on colloid retention are examined. In order to avoid full surface coverage effects, ultra-trace (30 ppb) Na-illite colloid concentrations are used. Laser-induced breakdown detection is applied in order to detect and quantify the Na-illite colloids. The results are directly compared to the experiments of Stoll, et al. [1] who investigated the transport and surface interaction of carboxylated polystyrene spheres (25 and 1000 nm diameter) using the same experimental setup and conditions. It is concluded that polystyrene spheres are no ideal analogue to predict the mobility and transport behavior of a polydisperse clay colloid suspension. Despite the higher solid density, the Na-illite colloids show higher mobility compared to the polystyrene spheres without significant impact of surface roughness or gravity. The platelet shape, the non-uniform surface charge distribution and slower sedimentation may account for the observed differences.

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http://dx.doi.org/10.1016/j.colsurfa.2017.05.067
Received 26 March 2017; Received in revised form 17 May 2017; Accepted 22 May 2017

1. Introduction

Colloids are ubiquitous in surface and subsurface waters. Due to the high diversity in both organic and inorganic forms (e.g. clay colloids, humic substances and viruses/bacteria) and their transport and surface interaction behavior, colloids have become an important subject in environmental research for decades [2]. Contaminant transport in groundwater [3–6], colloid facilitated radionuclide transport [7–10], pore clogging [11,12] and the local alteration of physical properties (e.g. permeability) due to the presence of clay material [13,14] are amongst other things, issues of current research. In the subsurface colloids are transported in porous and fractured media. Especially fractures serve as preferential conduits for colloids. This is due to (i) large apertures that enable high flow velocities compared to the surrounding rock matrix, (ii) mostly unfavorable conditions for attachment due to negatively charged surfaces of colloids and fracture walls under the circumneutural pH range expected in natural groundwater systems and (iii) negligible matrix diffusion of colloids in contrast to solutes [3,15–17]. Colloid transport through both artificial and natural fractures has been studied extensively in the past [18–20]. Because of constant and well defined material properties (e.g. defined geometry, monodisperse size, surface charge and low density) surface functionalized polystyrene spheres are often used as an analogue for natural colloids [21,22]. However natural colloids show irregular shapes, higher densities and a heterogeneous surface charge distribution impacting the transport behavior.

Studies comparing colloids of different materials have been carried out amongst others by Zvikelsky, et al. [23] and Albarran, et al. [24]. Zvikelsky, et al. [23] compared 1 μm latex microspheres with a polydisperse clay suspension (mean colloids size 1.34 μm) in transport experiments through a chalk rock fracture of 38.5 cm length. The results showed a lower clay colloid recovery compared to the latex spheres and a decrease in the mean colloid size of the mobile colloid fraction. Therefore, the authors accounted the higher density of the clay colloids for the observed colloid deposition and colloid size fractionation. Additional parameters possible triggering the colloid retention might be variable surface charge, irregular particle shape and polydispersity. The increase of colloid recovery while repeating the experiments was explained with full surface coverage because of the preceding experiments. This in turn results in fewer sites available for attachment. In the study of Albarran, et al. [24] the transport behavior of gold (40 nm and 100 nm), latex (30 nm, 115 nm, 220 nm and 500 nm) and smectite (< 500 nm) colloids in artificial granite fractures of 16–26 cm length under unfavorable attachment conditions was investigated (pH 7–10 and ionic strength of 5E–4 M $NaClO_4$). In contrast to Zvikelsky, et al. [23], higher colloid recovery of clay colloids compared to the latex and gold colloids of comparable sizes was observed. These results were attributed to the nature of the clay colloids: the charge distribution and the platelet shape. Apart from the different colloid sizes investigated in both studies, the observed deviations mentioned are most likely attributed to the substrates used. A chalk rock differs significantly in porosity, structure and Ca content from granite as substrate. Chrysikopoulos and James [25] investigated numerically the transport behavior of monodisperse and polydisperse colloid suspensions in water saturated, two-dimensional fractures with different spatially variable, anisotropic aperture topographies. They found that the colloid plume of a polydisperse colloid suspensions shows a higher spreading in contrast to monodisperse ones. Additionally, under the assumption of spherical colloids they show that the retention of dense colloids is higher in contrast to buoyant ones.

Against this background, contrasting features between colloids of different materials need to be considered and the appropriateness of polystyrene spheres as analogues needs to be verified. In this respect, the present study is an extension to the work of Stoll, et al. [1], which examined the transport of fluorescent carboxylated polystyrene spheres (CPS) through an artificial parallel-plate fracture flow cell under laminar flow conditions (7 mL/h) using fluorescent spectroscopy. In those transport experiments at pH 5 and 1 mM NaCl background electrolyte, the influence of colloid size and surface roughness on colloid retention was investigated under varying parameters like residence time, colloid size, collector material and fracture orientation. Despite the low density of CPS of 1050 kg/m^3, it could be shown that large 1000 nm CPS undergo sedimentation and deposition on the surface with increasing residence time while collector interaction is not affected by surface roughness variation. In contrast, for the investigated 25 nm CPS diffusion controlled transport dominated during stop flow conditions and collector interaction appears to be controlled by surface inhomogeneities such as surface roughness. In this particular case, the surface roughness was measured by atomic force microscopy on an area of 64 μm^2 (root mean square roughness of granodiorite ≈ 350 nm and of acrylic glass ≈ 20 nm).

The aim of this study is to interrogate the use of low density CPS as appropriate analogues to simulate natural clay colloids. For this purpose, identical experimental conditions and setup as presented in Stoll, et al. [1] are used to perform experiments with polydisperse clay colloids (illite) spanning the size range 35–350 nm. Consequently, the experiments are carried out under laminar flow conditions (7 mL/h), a background electrolyte of 1 mM NaCl at pH 5. For crystalline systems the pH values vary over a large range (pH 5 to pH 9.6) [26]. In this study and in the previous study we have chosen the lower end of the value range (pH 5) in order to investigate the effect of potential surface charge heterogeneities expected for crystalline rock. For detection and quantification of the clay colloids in the transport experiments Laser-Induced Breakdown Detection (LIBD) is applied. LIBD serves at this point as an alternative to light scattering techniques, which are frequently used to detect non-fluorescent particulate and colloid tracers in comparable experiments [e.g. 24]. Due to Rayleigh scattering in the size range of < 100 nm, light scattering techniques require comparatively high solid concentrations, which in turn might result in significant to full collector surface coverage. Additionally, such high colloid concentrations do not reflect natural groundwater colloid load. LIBD is developed to detect and quantify colloid sized particles at ultra-trace concentrations down to ppt-levels. Therefore, a high colloid load is not required, and the afore mentioned side effects like surface coverage are not an issue. Thus, in contrast to light scattering techniques, experiments under more natural conditions can be conducted using LIBD.

2. Material and methods

2.1. Synthetic fracture flow cell and experimental setup

The synthetic fracture flow cell and experimental setup are schematically shown in Fig. 1. A parallel-plate type fracture flow cell made of acrylic glass (Polymethyl methacrylate, PMMA, Plexiglas®) is used for the transport experiments. One fracture side always consists of acrylic glass and the opposite side material is exchangeable. Here either granodiorite or acrylic glass is used. The granodiorite from the Grimsel test site from the Aar Massif in Switzerland was cut using a diamond-studded saw blade. No further treatment on the disc was undertaken. The acrylic glass disc with identical dimensions has a cut and polished surface. Using streaming potential measurements (Anton Paar) both collector surfaces show negative overall zeta potentials under the experimental conditions (1 mM NaCl, pH 5.0 ± 0.1): Grimsel granodiorite −38 mV and acrylic glass −49 mV. The penny shaped fracture between both fracture sides is 38.3 mm in diameter with a constant aperture of 0.75 mm and a void volume of 0.86 mL. Including inlet and outlet channels within the acrylic glass it adds up to 0.99 mL. Further information on the granodiorite, the acrylic glass disc, and the fracture flow cell are detailed in Stoll, et al. [1].

In order to minimize potential colloid sorption in the experimental setup PEEK (Polyether ether ketone) tubing is used whenever possible [28]. The inlet of the fracture flow cell is connected to the colloid/