Stability of Silica Colloids Released from Injection Grout Silica Sol – 14130

Pirkko Hölttä *, Jukka Lehto *, Risto Harjula *
* Department of Chemistry, University of Helsinki, Finland

ABSTRACT

Colloidal silica, silica sol, is being used in the underground rock characterization facility ONKALO in Olkiluoto, Finland, for the sealing of the fractures of the hydraulic apertures less than 0.05 mm. The use of all colloidal material has to be considered in the long–term safety assessment of a spent nuclear fuel repository. The objective of this work was to follow the stability of silica colloids released from the gelled silica sol. Release and stability of silica colloids was studied in reference groundwaters, low salinity Allard and saline OLSO which simulates Olkiluoto conditions. Sodium and calcium chloride solutions and deionized water were used to study the stability of silica colloids as a function of ionic strength. The stability of colloids has been followed so far six years by measuring particle size distribution, colloidal silica concentration and zeta potential using dynamic light scattering. In the Allard water and in the most diluted sodium and calcium chloride solutions, the mean particle diameter has been rather constant at about 100 nm over the entire experimental time period. The highly negative zeta potential values have been indicated the existence of stable silica colloids. In the OLSO water and in 0.1 – 1 M sodium chloride and 0.03 – 3 M calcium chloride, the mean particle diameter has been increased during the experiment and the particle diameter has varied from nanometers to thousands of nanometers. Zeta potential values have been near zero, and an increase in particle size followed by the disappearance of large particles is an indication of particle flocculation or coagulation and unstable colloidal dispersion. Results confirmed that the stability of colloids depends significantly on the groundwater salinity. Under the prevailing saline groundwater conditions in Olkiluoto, silica colloids are instable, but the possible change in salinity e.g. due to glacial melt waters has to be considered.

INTRODUCTION

In Finland the final disposal of spent nuclear fuel is investigated by Posiva Oy in Olkiluoto utilizing the underground rock characterization facility ONKALO. The project seeks to obtain information about the bedrock at the site planned for the final disposal repository and assess its safety and test final disposal technology in actual deep underground conditions. Cement is typically used for permeation grouting in hard rock. Because high pH can be harmful for the Engineered Barrier System (EBS) and cement-based grouts may have limited penetration, non-cementitious grouts have been tested for the sealing of fractures with a small hydraulic aperture. Colloidal silica called silica sol manufactured by Eka Chemicals in Bohus, Sweden [1] will be used for the sealing of the fractures of the hydraulic apertures of 0.05 mm or less. The main experiences with colloidal silica come from geotechnical applications like the grouting of soil to increase its liquefaction resistance [2] and to seal narrow fractures in low permeable rock to prevent water leakage into tunnels [3, 4]. Silica sol-gel is sufficiently stable to limit water ingress during the operational phase. The requirement that the pH of groundwater in the repository should not exceed 11 is fulfilled and the compatibility with EBS materials is expected to be good [5, 6].

Colloid-facilitated transport of radionuclides may significantly contribute to the long–term

performance of a spent nuclear fuel repository. Several studies have indicated radionuclide (especially actinide) sorption on colloids and the mobility of radiocolloids. Field-scale studies at hazardous waste sites have evidenced that colloid transport can enhance actinide migration [7, 8]. Laboratory experiments confirmed that colloids can accelerate the transport of cationic and anionic metals through porous and fractured media [9–11]. In Olkiluoto, the determined natural inorganic and organic colloid contents in groundwater are low – less than 1 ppm – but the bentonite buffer used in the EBS system is assumed to be a potential source of colloids [12, 13]. However, the use of all colloidal material has to be considered in the long–term safety assessment of a spent nuclear fuel repository. The potential relevance of colloid-facilitated radionuclide transport is highly dependent on their stability in different geochemical environments. Objective of this work was to study release and stability of silica colloids in different groundwater conditions.

EXPERIMENTAL

Materials

The silica sol and NaCl accelerator being used by Posiva has the brand name "MEYCO$^{®}$ MP320" [1]. Silica sol is manufactured from quartz and NaCl. It is a stable suspension of amorphous particles of silica [SiO_2], which builds randomly, distributed [SiO_4]$^{4-}$ tetrahedra [14]. The particles have hydroxylated surfaces and are insoluble in water. The colloidal particle size is 5–100 nm. The average pH of the solution is 9.4 and viscosity of the sol is similar to water. To use silica sol as a grout, the particles have to aggregate and form a gel within a predictable time by using saline solution. The used concentration of the accelerator depends on the properties of the bedrock to be stabilized as groundwater flow, water temperature, the salinity of the surrounding water, and on the time required for the sol to gel. Higher salt concentration and temperature result in a shorter gelling time for the sol. In the experiments, the proportion of the NaCl accelerator was 20% corresponding 30 min initial setting and 45 min final setting times.

Gelled silica sol samples were made by mixing 4 mL silica sol and 1 mL accelerator in a 15 mL and 17 mm in diameter plastic centrifuge tube. After 45 min final setting time, 10 mL of reference groundwater or electrolyte solution were added on top of silica sol gel and the samples were stored in contact with a solution. The contact area for water and silica sol gel was 2.27 cm^2. Allard, low salinity granitic (I = 4.2 10^{-3} M) and OLSO, saline Olkiluoto (I = 0.517 M) reference groundwater were used as a leaching solutions with adjusted pH values 7–11. Electrolyte solutions, NaCl (I = 1 M – 1·10^{-7} M) and CaCl$_2$ (I = 3 M – 3·10^{-7} M) and deionized water (MilliQ) were used to study the stability of silica colloids as a function of ionic strength. Release and stability of colloids from gelled silica sol was determined after one month and then twice or once a year by analysing the particle size distribution, particle concentration and zeta potential.

Methods

Colloid particle size distribution and zeta potential were determined using Malvern Zetasizer Nano ZS equipment applying dynamic light scattering (DLS). Dynamic light scattering is a method based on the analysis of the temporal fluctuation of the scattered laser light intensity originating from the Brownian movement of dispersed particles [15, 16]. The intensity of the scattered light strongly depends on the hydrodynamic particle diameter which is an equivalent sphere diameter derived from a measurement technique involving hydrodynamic interaction between the particle

and fluid. Zeta potential is a measure of the magnitude of the repulsion or attraction between particles. An electric field is applied across the dispersed particles, which will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential. The frequency shift of an incident laser beam caused by moving particles is measured as the particle mobility which is converted to the zeta potential by the application of mathematical theories.

Colloidal particle concentration was estimated applying Zetasizer count rate and calibration using a standard series prepared from original silica sol solution. The count rate is roughly proportional to the concentration of particles and can be used to estimate colloid concentrations. The calibration curve was constructed by measuring known concentrations of particles with the same size as the colloids in the samples. Aerosil$^{®}$ EG50 high purity hydrophilic silica was used as a reference material. Colloidal silica concentration was also determined from total silicon concentration minus dissolved reactive silicate concentration e.g. monomers and lower oligomers. Dissolved reactive silica concentration was determined using molybdate blue (MoO_4) method [17]. Monomeric silica reacts with molybdate reagent in acid media to form a yellow silico-molybdate complex. This complex is reduced by ascorbic acid to form the molybdate blue color. The color intensity determined by UV/VIS spectrophotometer is proportional to the silica concentration. Total silica concentrations were determined using ICP–MS spectrometry.

RESULTS AND DISCUSSION

Release of silica colloids was followed by analysing pH, particle size distribution, colloidal particle concentration and zeta potential for six years. After one month, pH values differed remarkably from initial pH values (7–11). At the beginning, pH was stabilized predominantly due to atmospheric CO_2. After three years, measured pH values were increased and stabilized likely due to hydroxide ions produced in the dissolution of silica. Difference in pH values between OLSO (8.2 $\pm$ 0.2) and Allard (9.4 $\pm$ 0.2) is explained by calcium and sodium ions present in saline OLSO in which calcium- and sodium hydroxide is produced resulting in lower pH values. In NaCl and $CaCl_2$ solutions, stabilized pH values were dependent on ionic strength. After three years, mean pH value in 10^{-7}–0.01 M NaCl solutions was 9.4 $\pm$ 0.1, in 0.1 M NaCl solution 9.1 $\pm$ 0.1 and in 1 M NaCl solution 8.5 $\pm$ 0.1. Mean pH value in $3 \cdot 10^{-7}$– 0.003 M $CaCl_2$ solutions was 9.4 $\pm$ 0.1, in 0.03 M $CaCl_2$ solution 8.5 $\pm$ 0.1, in 0.3 M $CaCl_2$ solution 8.2 $\pm$ 0.1 and in 3 M $CaCl_2$ solution 7.2 $\pm$ 0.1. In deionized water, mean pH value after three years was 9.5 $\pm$ 0.1.

Colloid Size

Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids as a function of time in Allard reference groundwater is presented in Figure 1 and in OLSO reference groundwater in Figure 2. The results are given as a mean value of five parallel samples. DLS is very insensitive to small particles in the presence of larger sized particles because the major part of the scattering light intensity is produced by large particles [15]. In Allard reference groundwater, the mean particle diameter was around 100 nm and the colloid size distribution has been rather constant during the following time. In saline OLSO samples, the mean particle size distribution is wide, from nanometers to thousands of nanometers. Small particle sizes indicated that reversible flocculation or irreversible coagulation had taken place.
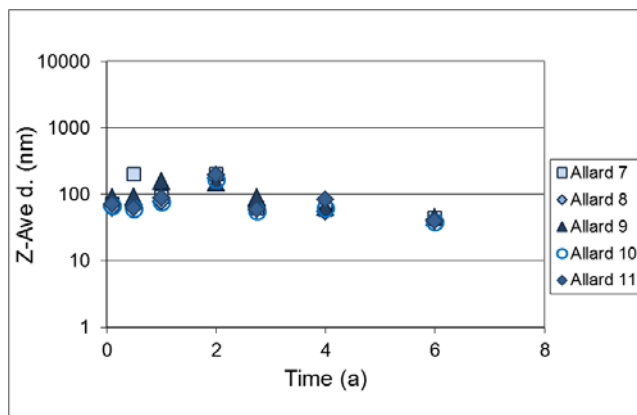
Fig. 1. Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids in Allard reference groundwater (initial pH 7-11) as a function of time.
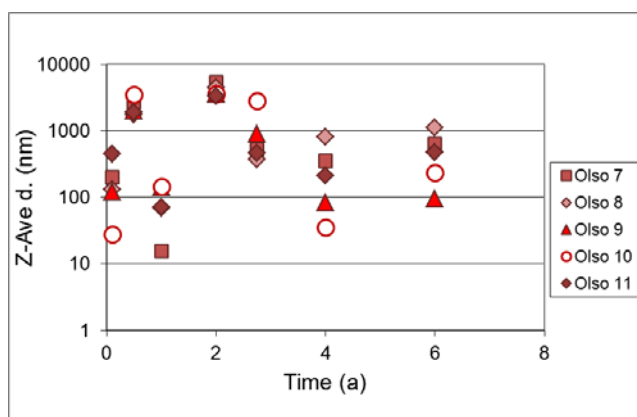

Fig. 2. Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids in OLSO reference groundwater (initial pH 7-11) as a function of time.

Mean particle diameter of released silica colloids as a function of ionic strength in NaCl solutions is presented in Figure 3 and in $CaCl_2$ solutions in Figure 4. Mean particle diameter of released silica colloids as a function of time in NaCl solutions is presented in Figure 5 and in $CaCl_2$ solutions in Figure 6. In 10^{-7}– 0.01 M NaCl and 3 10^{-7}– 0.003 M $CaCl_2$ solutions, the mean particle diameter of released silica colloids was around 100 nm and the colloid size distribution was rather constant like in the Allard samples. In 0.1 – 1 M NaCl and 0.03 – 3 M $CaCl_2$ solutions, the particle size distribution was wide from a nanometer scale to thousands of nanometers indicating particle aggregation and parallel reversible flocculation or irreversible coagulation. The stability of silica colloids depended also on the valence of the cations in the solution. In monovalent sodium chloride solution colloids were stable when the ionic strength was 0.01 M or lower. In divalent calcium chloride solution colloids were only stable in the ionic strengths of 0.003 M or under.
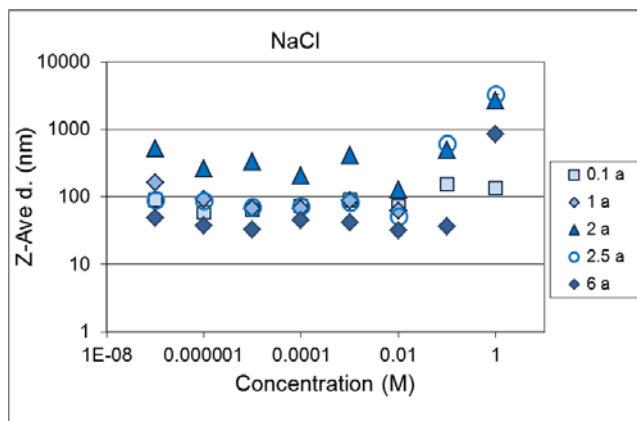
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Fig. 3. Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids in NaCl solutions as a function of ionic strength.
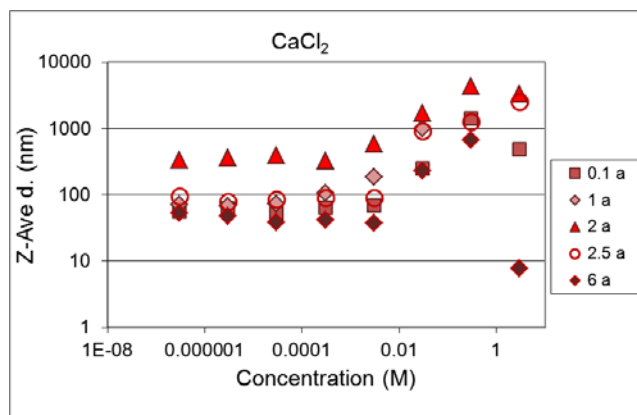

Fig. 4. Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids in $CaCl_2$ solutions as a function of ionic strength.
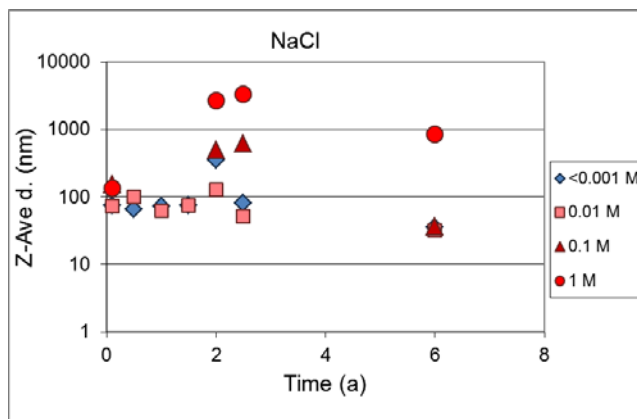

Fig. 5. Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids in NaCl solutions as a function of time.
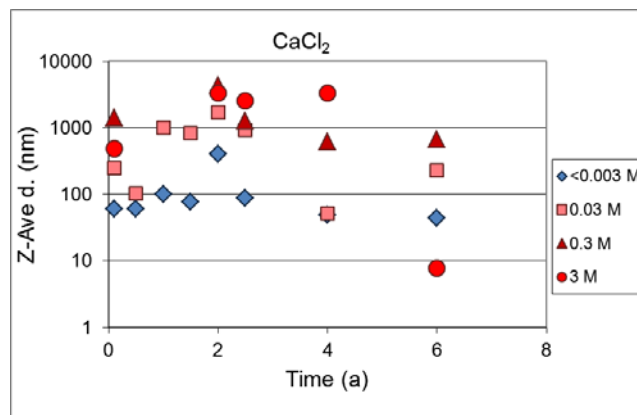
Fig. 6. Mean hydrodynamic particle diameter (*Z-Ave d*) of released silica colloids in $CaCl_2$ solutions as a function of time.

Colloid Concentration

Particle concentration of released colloids was estimated applying Zetasizer parameter derived count rate and a standard series. Released particle concentration was normalized to the contact area for water and silica gel. Mean released particle concentration in OLSO samples taken after six years was 4.0 ± 2.8 ppm·cm^{-2} and in Allard samples 13.3 ± 3.2 ppm·cm^{-2}. Corresponding particle concentration in dilute NaCl (10^{-7}– 0.01 M) solutions was 8.9 ± 4.0 ppm·cm^{-2} and in dilute $CaCl_2$ ($3 \cdot 10^{-7}$– 0.003 M) solutions 8.7 ± 2.2 ppm·cm^{-2}. In both solutions particle concentrations were rather constant over an experimental time period. The concentrations of the released silica colloids were slightly higher than concentrations of natural colloids determined in granitic groundwaters. In 0.1 – 1 M NaCl and 0.03 – 3 M $CaCl_2$ solutions particle concentrations were low due to the aggregation of colloids and an inaccurate determination method. Colloid concentration estimated by DLS is not very accurate. The accuracy of DLS determinations is dependent on the size and geometrical shape of the colloids. The colloids used in the calibration curve are spherical, which is not appropriate for aggregated silica colloids in OLSO water. Mean particle concentrations calculated from total silica minus dissolved reactive silicon concentration were slightly higher than estimated from Zetasizer measurements. The appearance and kinetics of reactive and colloidal silica under geologically relevant aqueous conditions are very complicated and depend on the degree of supersaturation, ionic strength and pH of the solutions.

Colloid Stability

Mean zeta potential of released silica colloids as a function of time for Allard reference groundwater is presented in Figure 7 and for OLSO reference groundwater in Figure 8. Corresponding results for NaCl solution is presented in Figure 9 and for $CaCl_2$ solution in Figure 8. In a stable dispersion, all suspended particles have a large negative or positive zeta potential and they will tend to repel each other. The colloidal system is least stable near the isoelectric point where zeta potential is near zero and there is no force to prevent the particles from aggregating. In high salt concentrations, initial aggregation (flocculation) can be reversible and weak flocs may dissociate under an externally applied force such as vigorous agitation. The particles in colloidal dispersion may adhere to one another and form aggregates of successively increasing size that separates out by sedimentation. High negative zeta potential

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values indicated the existence of rather stable silica colloids. After six years, in OLSO reference groundwater like in 0.1 –1 M NaCl and 0.03 – 3 M $CaCl_2$ solutions, zeta potential values were around zero indicating particle aggregation and instable colloids. In Allard reference groundwater and in dilute electrolyte solutions, mean zeta potential values were lower than -30 mV, indicating stable colloid dispersion. According to this study, the threshold value of ionic strength is 0.03–0.1 M when salinity has an effect on the stability of colloids. Groundwater conditions in Olkiluoto are from medium saline to saline. The ionic strength of saline groundwater is order of magnitude higher than the threshold value range for ionic strength obtained in this study.
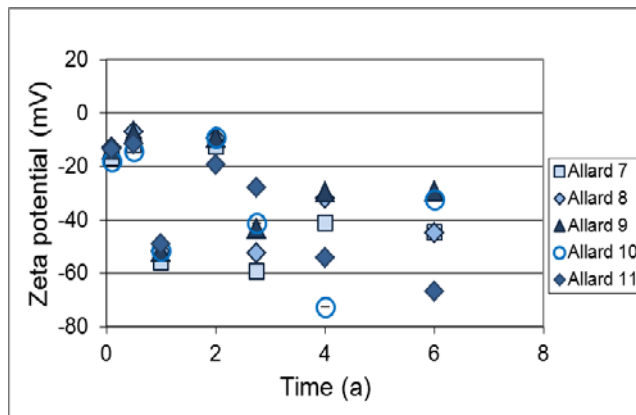

Fig. 7. Mean Zeta potential of released silica colloids in Allard reference groundwater (initial pH 7-11) as a function of time.
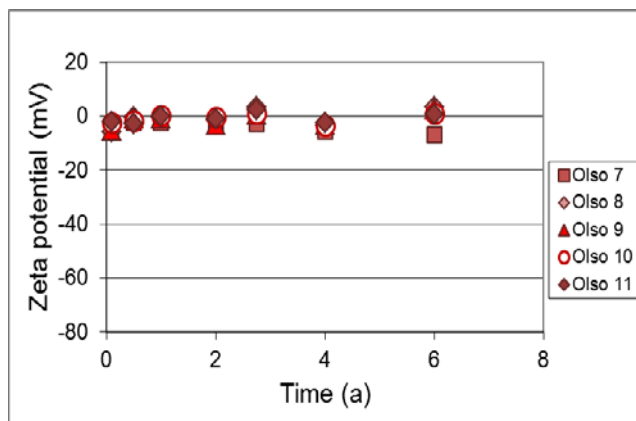

Fig. 8. Mean Zeta potential of released silica colloids in OLSO reference groundwater (initial pH 7-11) as a function of time.
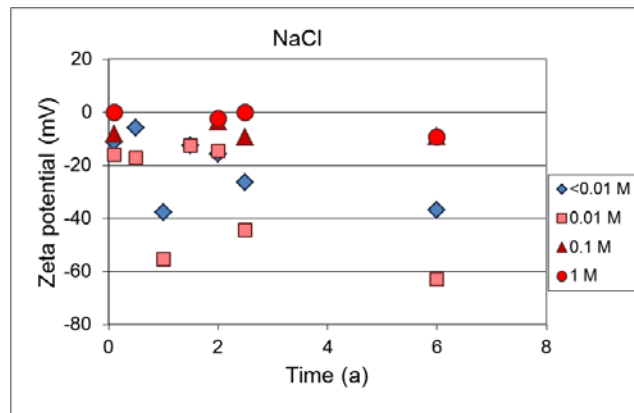
Fig. 9. Mean Zeta potential of silica colloids in NaCl solutions as a function of time.
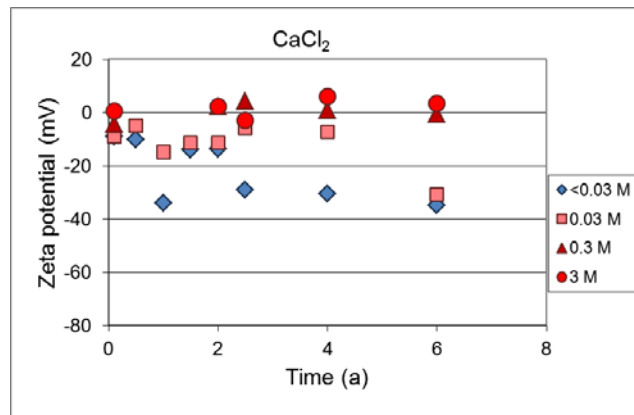

Fig. 10. Mean Zeta potential of silica colloids in $CaCl_2$ solutions as a function of time.

CONCLUSIONS

The use of colloidal silica sol for permeation grouting must be considered in the long-term safety assessment of a spent nuclear fuel repository. In this work silica colloid release from gelled silica sol and stability of colloids in different groundwater conditions was determined. The stability of silica colloids was found to be dependent significantly on groundwater salinity. In saline reference groundwater OLSO and in 0.1–1 M NaCl and 0.03–3 M $CaCl_2$ solutions particle size distribution was wide from a nanometer scale to thousands of nanometers. Zeta potential values of colloids were around zero indicating favorable conditions for particle aggregation and instability of colloids. After six years, in low salinity reference groundwater Allard and dilute electrolyte solutions, mean particle diameters were less than 450 nm. Rather constant particle size distribution and high negative zeta potential values indicated the existence of stable silica colloids. The potential relevance of colloid-facilitated radionuclide transport is dependent on colloid stability and mobility in different geochemical environments. Under prevailing medium saline to saline groundwater conditions in Olkiluoto no significant release of colloids from silica sol is expected but the possible influence of glacial melt waters has to be considered.

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ACKNOWLEDGEMENTS