

**Natural Colloids in Groundwater from a Bentonite Mine
- Correlation between Colloid Generation and Groundwater Chemistry -**

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ABSTRACT

Colloids, mainly montmorillonite, generated by erosion of compacted bentonite by groundwater flow might enhance the transport of radionuclides from a radioactive waste repository. The influence of aqueous chemistry (i.e. pH, cation concentration and valence) on the dispersion of montmorillonite colloid was studied. Colloids were flocculated under higher cation concentrations ($[\text{Na}^+] > 10^{-2} \text{ M}$, $[\text{Ca}^{2+}] > 10^{-3} \text{ M}$) and/or under acidic condition (pH = 4) by means of batch-type experiments. Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was applied to estimate the stability of colloidal dispersion and then the limitation of theoretical calculations was pointed out. Groundwater samples were collected from two galleries at different depths of the Tsukinuno bentonite mine (northern Honshu, Japan) and investigated for the populations of colloids. The groundwater flows vertically through Tertiary sedimentary argillaceous rocks and fine tuff beds which are mined for bentonite. Low colloid concentrations were measured in these groundwater samples. This result suggests that the colloids cannot significantly disperse in the groundwaters under higher cation concentration ($[\text{Na}^+] > 10^{-2} \text{ M}$) or under acidic conditions. This result is consistent with those of the batch-type experiments.

INTRODUCTION

Groundwater colloids may act as carriers for sorbing radionuclides released from a radioactive waste repository [1]. Since the stability of colloidal dispersion is affected by factors such as pH, ion concentration and valence in the solution, the characterization of groundwater colloids in deep aquifers has been performed considering the correlation between colloid concentration and groundwater chemistry [2]. With regard to colloidal effects on radionuclide transport, the properties of bentonite are of prime importance since it is the primary candidate as buffer material of geological disposal of high-level radioactive wastes considered by various regulatory agencies. The buffer swells when saturated by groundwater and colloidal particles could be generated [3, 4]. The transport of radionuclides sorbed on these particles may be accelerated due to the fast transport of particles. In order to estimate the stable conditions for the colloidal dispersion of bentonite we conducted a series of batch-type experiments and investigated natural colloids suspended in groundwater falling individual droplets from the top of a gallery in a bentonite mine located in Japan. The chemical conditions of groundwater to

maintain the colloidal dispersion are discussed from the results of laboratory experiments and field study.

EXPERIMENTAL

Batch-type experiments on colloid suspending

We used an industrially refined Na-type bentonite, 'Kunipia-F', manufactured by Kunimine Industries Co. Ltd. The montmorillonite content is higher than 99%. Aliquots of bentonite powder were soaked in different solutions, distilled water, NaCl (10^{-3} - 10^{-1} M) and CaSO₄ (10^{-5} - 10^{-3} M) with a bentonite/solution ratio of 500 mg/L. The bentonite suspensions were stirred for 24 hours. The pH of solutions was adjusted to ~9 and ~4 by adding NaOH and HCl, respectively. The upper clear solutions were collected after 2 and 7 weeks settling and were filtrated using ultrafilters with effective 10000 molecular weight cutoffs (MWCO). The concentrations of Si, Al and Mg of solutions and filtrates were analyzed by ICP-AES in order to evaluate the concentration of suspended montmorillonite colloids.

Electrophoretic measurements

The stability of colloidal dispersion is related to the surface potential of particles. It increases with increasing absolute value of surface potential since the electrostatic repulsion between the particles also increases [5]. To establish the stable conditions for the colloid suspension of montmorillonite, we measured the surface potentials (zeta potentials) of particles by using the electrophoresis method. To evaluate the pH dependency on the zeta potentials, the suspensions were prepared in 10^{-2} M NaCl solutions with various pHs ranging from 4 to 11 by adding HCl or NaOH.

Natural colloids suspended in groundwater percolating through a bentonite deposit

As a natural analogue study of groundwater colloids suspended around the near-field of a waste repository, we investigated groundwater percolating through the Tsukinuno bentonite deposit (northern Honshu, Japan). The bentonite beds which are several to several tens centimeters thick are interbedded with shales. The beds are composed primarily of Na-type montmorillonite and quartz with low amounts of plagioclase and calcite [6]. Figure 1 shows a geologic section through the deposit. The sequence is composed of marine sedimentary rocks including sandy tuff, bentonite-bearing shales and mudstones. The age of sedimentation ranges from 14 to 8 million years [7]. The bentonite is mined in several galleries. We collected two samples of groundwater which is falling individual droplets from a bentonite-shale boundary at the top of the gallery. Water was also collected on the surface and above the deposit (Fig. 1). During the sampling, no muddiness was noticed in these samples A, B and C and they have been analyzed for concentration of ions and colloids. The same protocol was applied for natural water samples and the solutions of batch-type experiments to evaluate the colloid concentration.

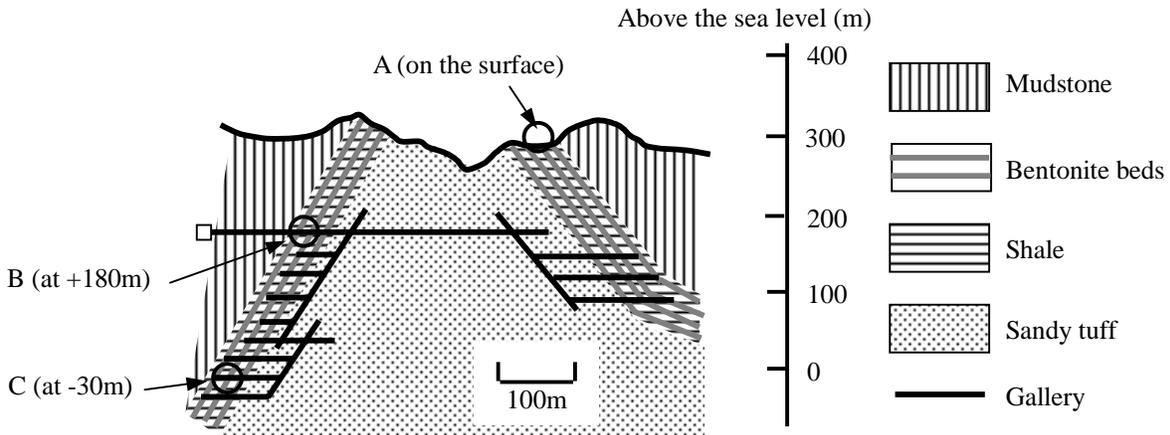


Figure 1. Schematic cross section through the Tsukinuno bentonite mine, northern Japan. Locations of sampled groundwater (A - C) and their depths (above the sea level) were indicated.

RESULTS AND DISCUSSION

Stability behavior of colloid suspension

The concentrations of montmorillonite colloids, analyzed by a series of batch-type experiments under various chemical conditions, are reported in Figure 2 (pH 9) and Figure 3 (pH 4). The stability of colloid dispersion depends on the cation concentration because the electric double-layer of the particle surface, caused by its negative charge, is compressed by the cations in the solution [5].

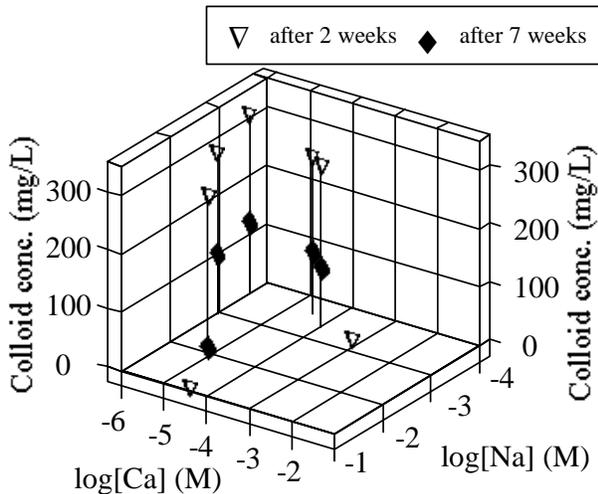


Figure 2. Concentration of montmorillonite colloids at pH9 as a function of Na and Ca concentrations. Initial concentration of suspended particles is about 500mg/L.

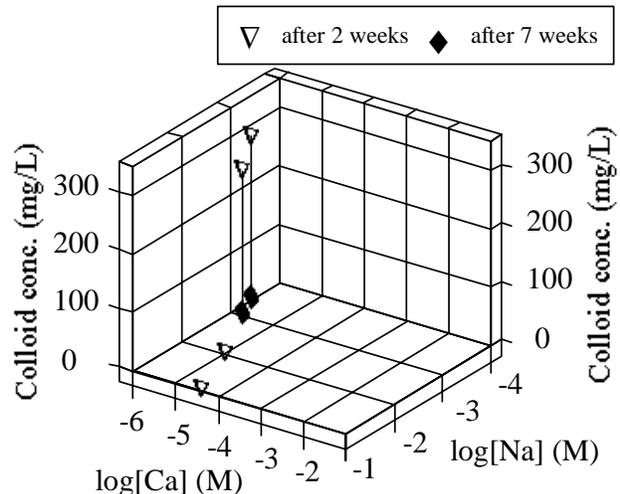


Figure 3. Concentration of montmorillonite colloids at pH4 as a function of Na and Ca concentrations. Initial concentration of suspended particles is about 500mg/L.

At pH 9 (Fig. 2), a remarkable amount of suspended particles (> 100 mg/L) was confirmed in some experimental solutions (i.e. distilled water, 10^{-3} M NaCl, 10^{-5} M CaSO₄ and 10^{-4} M CaSO₄ solutions) even after 7 weeks settling. The dispersive stability of suspended particles seems to be maintained in these solutions. On the other hand, the amount of colloids is lower when the cation concentrations are higher ($[Na^+] > 10^{-2}$ M, $[Ca^{2+}] > 10^{-3}$ M) because almost all particles were flocculated after 7 weeks settling. Furthermore, colloidal suspensions were unstable in solutions whose pH was adjusted to 4 (Fig. 3). The colloids were flocculated after 7 weeks settling even though the ion concentration in the solution was sufficiently low to maintain the colloidal dispersion. These results indicate that montmorillonite colloids are flocculated when the Na⁺ concentration of the solution is higher than 10^{-2} M and/or when the Ca²⁺ content is higher than 10^{-3} M. The dispersive stability was also decreased by the acidity of the solution (i.e. pH 4). In case of saline or acidic groundwater, montmorillonite colloids are expected to be flocculated.

Electrostatic properties of montmorillonite particle and prediction of colloid dispersion

The zeta potential of montmorillonite particles was measured to predict the stability of colloid suspension. Bentonite particles are plate-shaped with two types of surfaces, namely face and edge. The face surface has a permanent negative charge generated by the substitution of lattice cations whereas the edge surface has a pH dependent charge caused by protonation/ /deprotonation behavior [8]. Therefore, the zeta potential of the edge surface should be obtained to predict the pH dependency of the stability of colloid suspension. The measured zeta potential, analyzed by using the electrophoresis method, is mainly ascribed to the faces of montmorillonite particles. Since the edge surfaces represent only a small fraction of total surfaces ($< 1\%$), it is difficult to directly analyze the zeta potential of the edges [9]. This is why we measured the zeta potentials of SiO₂ and Al₂O₃ powders in order to estimate that of edge surfaces, which are composed of silica and alumina sheets. According to the reported assumption [10], the zeta potential of edges can be estimated as an arithmetic mean of those of SiO₂ and Al₂O₃ :

$$\zeta(E) = \{\zeta(\text{SiO}_2) + 2\zeta(\text{Al}_2\text{O}_3)\}/3 \quad (\text{Equation 1})$$

The measured values of zeta potentials (on face surfaces) and the estimated values calculated from Equation (1) (at edge surfaces) are shown in Figure 4. The measured potential values were around -40 mV and were almost constant at different pHs in 10^{-2} M NaCl solution whereas the estimated potential values of the edges closely depend on the pH of the solution. The zeta potential of the edges is about 0 mV at pH 7. Since the point of zero charge of the edges is also estimated at pH 6.8 using the titration and back titration method [11], the pH dependency of the edge potentials seems to be appropriate.

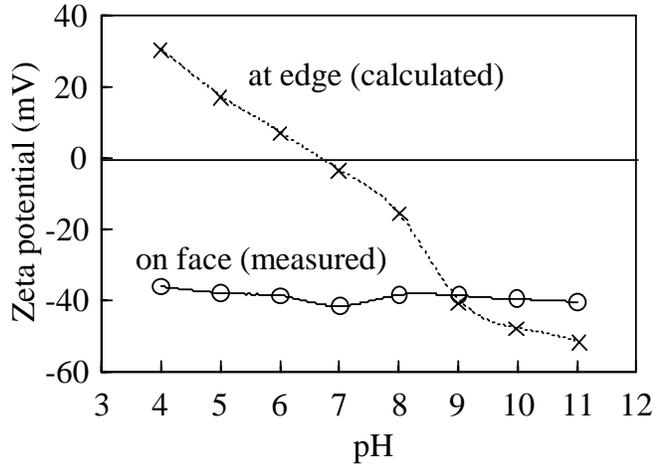


Figure 4. Zeta potential of montmorillonite particle as a function of pH in 10^{-2} M NaCl solution. The zeta potential at edge of the particle was calculated using Equation (1).

In order to predict a range of ion concentration to maintain the stability of colloidal dispersion, the DLVO theory has been generally used for calculations because of its effectiveness and convenience. The DLVO theory considers the van der Waals attraction and the diffuse double-layer repulsion as the potential energy of interaction between two particle surfaces. In this calculation, the geometry of particle surfaces was considered as flat plates and two different types of particle association, face-to-face (F/F) and face-to-edge (F/E), were assumed. The critical flocculation condition of colloids is estimated by the following equation [12] :

$$\phi(F)\phi(F) \text{ or } \phi(F)\phi(E) = 3.6 \times 10^{21} Az(c)^{1/2} \quad (\text{Equation 2})$$

where $\phi(F)$ and $\phi(E)$ are the surface potentials of face and edge, respectively. A is the Hamaker constant, z is the ionic valence and c is the electrolyte concentration in the solution. The products ($\phi(F)\phi(F)$ and $\phi(F)\phi(E)$) are the electrostatic interaction of the F/F and the F/E associations, respectively. When $\phi(F)\phi(F)$ or $\phi(F)\phi(E)$ is higher than $3.6 \times 10^{21} Az(c)^{1/2}$, the colloidal dispersion is predicted as a stable system because of the large repulsive interaction between the two surfaces. The critical flocculation condition predicted by Equation (2) is illustrated in Figure 5 (i.e. solid curves). The values of $z = 1$ and $A = 1 \times 10^{-19}$ J [13] were used for calculations. Since the area between two solid curves in these figures represents a flocculated condition for the colloids, the stability of colloidal dispersion tends to increase with decreasing concentration of monovalent cations in the solution. The obtained zeta potentials of montmorillonite particles, the face and the edge surfaces, were also plotted to evaluate the tendency of dispersive stability of colloids depending on the ion concentrations. The electrostatic interactions of the F/F and the F/E associations were compared with their related theoretical flocculation conditions.

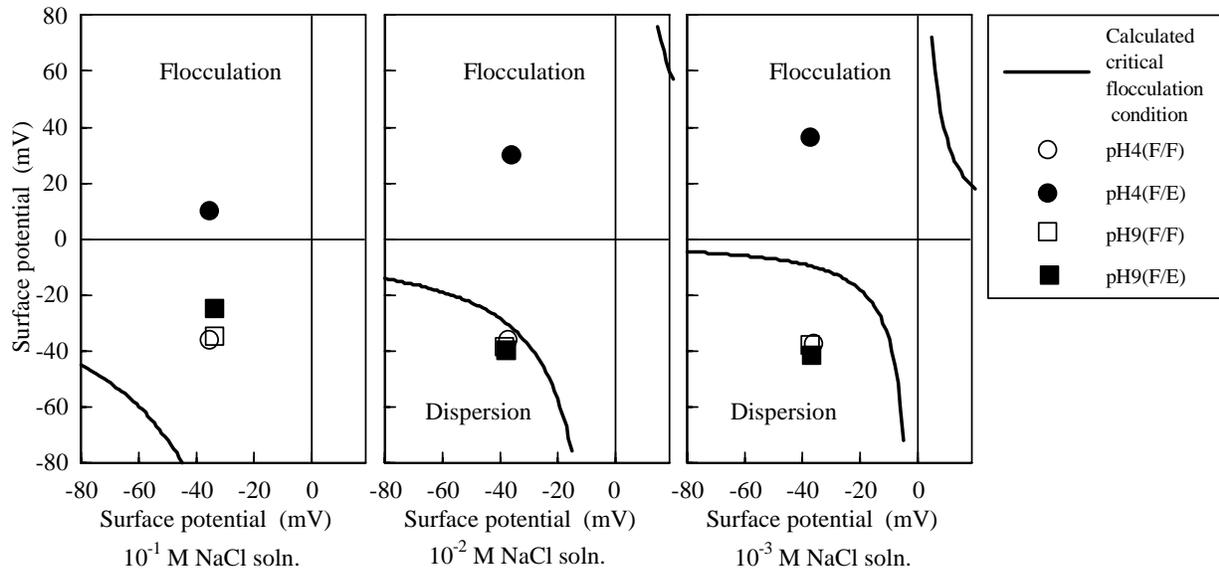


Figure 5. Relation between montmorillonite colloid dispersion and NaCl concentrations. The critical flocculation conditions are calculated for z (ionic valence) = 1 and A (Hamaker constant) = $1 \times 10^{19} \text{J}$ using Equation (2). The area between the two curves represents the flocculated condition. In order to evaluate the electrostatic interactions of face-to-face (F/F) and face-to-edge (F/E) associations, the potential values of the face and the edge at pH 4 and 9 are plotted, respectively. (face to face at pH 4 (○) ; face to edge at pH 4 (●) ; face to face at pH 9 (□) ; face to edge at pH 9 (■))

Montmorillonite colloid suspension is predicted to be unstable at pH 4 because of the positive charge of edge surfaces. This result is in good agreement with those of batch-type experiments which indicate that montmorillonite colloids are flocculated at pH 4. According to the result of zeta potential measurements (Fig. 4), these colloids could be flocculated under acidic conditions ($\text{pH} < 6$) due to the positive edge charge. At pH 9, the stability of colloidal dispersion is predicted to depend on the NaCl concentration between 10^{-1} M and 10^{-3} M . Montmorillonite colloid suspension is estimated to remain stable in a 10^{-2} M NaCl solution. From the results of batch-type experiments, however, we observed that suspended particles were flocculated in the NaCl solutions with concentrations of 10^{-1} M and 10^{-2} M . Therefore, there is a certain degree of disagreement between calculation and results of batch-type experiments [14]. Although the stability behavior of colloidal dispersion depending on pH and ion concentration may be interpreted by the DLVO theory in some cases, these results point out the limitation of theoretical calculations. The prediction implies some degree of uncertainty, likely because the theory does not take into account non-DLVO forces (e.g. hydration force of surfaces).

Natural colloids suspended in groundwater from the bentonite mine

Natural colloids suspended in groundwater percolating through the Tsukinuno bentonite deposit were investigated to understand the potential relation between colloid generation and groundwater chemistry. The chemical composition of the sample water is reported in Table I.

Table I. Chemical composition of the surface water and the groundwater

Samples Sampling depth (above the sea level)	A about 300m (on the surface)	B 180m	C -30m
pH	7.0	4.0	8.7
Concentration (M)			
Na ⁺	4.5 x 10 ⁻⁴	3.9 x 10 ⁻³	4.3 x 10 ⁻²
K ⁺	4.4 x 10 ⁻⁵	1.1 x 10 ⁻⁴	9.5 x 10 ⁻⁵
Ca ²⁺	5.2 x 10 ⁻⁵	4.9 x 10 ⁻⁴	1.1 x 10 ⁻⁴
Mg ²⁺	9.9 x 10 ⁻⁶	3.4 x 10 ⁻⁴	3.4 x 10 ⁻⁵
HCO ₃ ⁻	8.2 x 10 ⁻⁵	0	1.7 x 10 ⁻²
Cl ⁻	1.6 x 10 ⁻⁴	1.6 x 10 ⁻⁴	2.3 x 10 ⁻³
SO ₄ ²⁻	1.8 x 10 ⁻⁴	2.5 x 10 ⁻³	1.0 x 10 ⁻²

The concentration of major ions (Na⁺, Cl⁻ and SO₄²⁻) tends to increase with increasing the depth of sampling locations. Natural colloids were not detected in these samples for which no muddiness was observed. The concentration of suspended particles is < 1 mg/L considering the detection limit of the ICP-AES. This is in good agreement with results of batch-type experiments which indicate that montmorillonite colloids are flocculated under high cation concentrations ([Na⁺] > 10⁻² M) and/or acidic conditions (pH 4). The concentration of monovalent cations in sample C is higher than 10⁻² M and the pH of sample B is 4. Therefore, the montmorillonite colloids are expected to be flocculated in these groundwater samples. The stream water (sample A) was collected on the surface and does not percolate through the deposit so that no detectable amount of particles seems to be generated. By analogy with colloid suspension around the near-field of a waste repository, montmorillonite colloids are expected to be flocculated in groundwater whose Na concentration is higher than 10⁻² M and flocculation will be enhanced by the occurrence of divalent cations. In case of acidic waters, particle aggregation might occur by the F/E association of montmorillonite particles.

CONCLUSIONS

Batch-type experiments were performed under various chemical conditions to evaluate the stable condition of colloidal dispersion of montmorillonite. By analyzing the colloid concentration, it appears that montmorillonite colloids were flocculated in solutions having higher cation concentrations ([Na⁺] > 10⁻² M, [Ca²⁺] > 10⁻³ M). The zeta potential of montmorillonite particles was analyzed to characterize the electrostatic property of their surfaces. The potential of face surfaces is considered to be negative due to a permanent charge whereas the potential of edge surfaces seems to be closely dependent on the pH of the solution. The edges of

montmorillonite particles were positively charged under acidic conditions ($\text{pH} < 6$) and therefore these colloids are easily flocculated by the face-to-edge associations. Although the stability behavior of colloidal dispersion may be interpreted by the DLVO theory in some cases, there is a certain degree of disagreement between theoretical calculations and experimental results, likely because non-DLVO forces were not taken into account in our calculations. Natural colloids in groundwater from a bentonite mine were also investigated as a natural analogue of colloid generation around the near-field of a waste repository. Since low colloid concentrations were measured, we suggest that colloids cannot significantly disperse in groundwater under higher cation concentration ($[\text{Na}^+] > 10^{-2} \text{ M}$) or under acidic conditions.

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