Investigating the Reversibility of Calcium and Sodium Ion-Induced Bentonite Colloid Aggregation Using Scattering Techniques

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Abstract

In geological disposal of high-level radioactive waste, bentonite is commonly employed as a buffer backfill material, and the existence form of its colloids in the deep repository environment may influence the adsorption, diffusion, and migration behaviors of key radionuclides. Using single-layer bentonite colloids as the research object, and combining synchrotron radiation X-ray small-angle scattering and dynamic light scattering techniques, the effects of typical cations Ca2+ and Na+ on the aggregation structure and aggregation reversibility of bentonite colloids were investigated at the nanometer to micrometer scale. The results indicate that Ca2+ may cause bentonite colloids to form face-to-face stacked periodic structures (d = 1.86 nm) through a "bridging" mechanism. Following dialysis with 8000-14000 kDa membranes, the micrometer-scale secondary aggregation structures were found to undergo partial deaggregation, while most periodic stacked structures persisted. Na+ can induce bentonite colloids to form loose edge-to-face aggregates, which completely dissociated into a single-layer state after dialysis. In solutions containing both Ca2+ (5 mM) and Na+ (30 mM), the aggregation mode of bentonite colloids is dominated by Ca2+. Based on the characteristics of Beishan groundwater, it can be inferred that in the repository environment, bentonite colloids in the near-field may remain in an aggregated state for extended periods, which would to some extent inhibit the migration of radionuclides adsorbed on bentonite colloids.

Full Text

Reversibility of Bentonite Colloid Aggregation Induced by Calcium and Sodium Ions: Insights from Scattering Techniques

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Abstract

[**Background**]: Stable and mobile bentonite colloids can adsorb various radionuclides and facilitate their migration. Therefore, a thorough understanding of the stability and aggregation behavior of bentonite colloids in groundwater environments is of great significance for accurately assessing the long-term safety performance of high-level radioactive waste disposal repositories. [**Purpose**]: This study aims to investigate the reversibility and mechanism of bentonite colloid aggregation induced by typical cations Ca^{2+} and Na^{+}. [**Methods**]: This study combined synchrotron radiation small-angle X-ray scattering and dynamic light scattering techniques to analyze the aggregation structure of single-layer bentonite colloids influenced by Ca^{2+} and Na^{+} at the nanoscale to microscale, and compared the structural changes before and after dialysis. [**Results**]: The results demonstrated that Ca^{2+} promoted the assembly of face-to-face aligned lamellar structures with a characteristic interlayer spacing of 1.86 nm, mediated by a distinctive ionic bridging mechanism. Following dialysis, only microscale secondary aggregates exhibited partial disaggregation, while the cyclic lamellar structures maintained their structural integrity. In contrast, Na^{+} promoted the formation of loosely packed edge-to-face aggregates that underwent complete dissociation into individual monolayers upon dialysis. In mixed Ca^{2+}-Na^{+} electrolyte systems, the colloidal aggregation behavior of bentonite was found to be dominantly controlled by Ca^{2+}. **Conclusions**: Considering the characteristics of the groundwater at the Beishan site, it can be inferred that bentonite colloids near the disposal site are likely to remain in an aggregated and sedimented state for long time, which to some extent inhibits the migration of radionuclides adsorbed onto the bentonite colloids.

Keywords: Bentonite colloids, Aggregation reversibility, SAXS, DLS

Introduction

The safe disposal of high-level radioactive waste represents a critical challenge constraining the sustainable development of nuclear energy. It is projected that by 2050, China will generate 6,600 tonnes of spent fuel annually, with cumulative production reaching 110,000 tonnes. The reprocessing of this fuel will yield substantial quantities of high-level radioactive waste. Deep geological disposal based on the multiple-barrier concept is considered the only feasible solution for safe management of high-level radioactive waste, and China has entered the

underground laboratory construction phase for geological disposal.

Buffer/backfill materials constitute a crucial component of the multi-barrier system for deep geological disposal of high-level radioactive waste, serving as an engineered barrier between waste canisters and the surrounding rock to ensure long-term safety and stability of the repository. Extensive research has demonstrated that bentonite, primarily composed of montmorillonite, is an excellent buffer/backfill material. China has designated the Gaomiaozi (GMZ) sodium-based bentonite from Inner Mongolia as the preferred buffer/backfill material. Compacted bentonite at the interface with fractured host rock can be eroded by groundwater to form colloids ranging from 1 to 1000 nm. Previous studies have shown that stable, mobile bentonite colloids can adsorb various radionuclides and facilitate their migration along fracture water. Therefore, investigating the occurrence forms of bentonite colloids in groundwater is essential for safety assessment of repositories.

Groundwater ionic strength, ion type, pH, and temperature significantly influence bentonite colloid stability. Bentonite colloids are unstable under high ionic strength and acidic conditions, with divalent cations exhibiting more pronounced aggregation effects than monovalent cations. Xian et al. investigated pH effects on GMZ bentonite colloid stability and proposed aggregation mechanisms based on edge charge distribution. Xu et al. found that alkaline conditions promote stability of GMZ bentonite colloids, whereas high temperature and high salinity have opposite effects, discussing Ca^{2+} and Na^{+} influences on sedimentation behavior through DLVO theory. Notably, long-term geological activities may reduce groundwater ionic strength through recharge from rivers, lakes, and rainfall. Consequently, studying the reversibility of bentonite colloid aggregation—whether aggregated colloidal clusters can revert to stable, mobile states under favorable ionic conditions—is critically important for repository safety assessment. However, research on bentonite colloid aggregation reversibility remains limited. Mayordomo et al. confirmed that reduced ionic strength facilitates disaggregation of aggregated FEBEX bentonite colloids, though particle size cannot fully recover. Xu et al. observed that in GMZ bentonite colloid systems containing Na^{+}, hydrodynamic diameter returns to initial levels after Na^{+} concentration reduction. Due to experimental design and methodological limitations, current understanding of bentonite colloid aggregation structures and reversibility remains inadequate.

This work combines dynamic light scattering (DLS) and synchrotron radiation small-angle X-ray scattering (SAXS) techniques to investigate the aggregation behavior of single-layer bentonite colloids across nanometer to micrometer scales, based on hydrodynamic diameter and local lamellar stacking structure parameters. We systematically compare the effects of Ca^{2+} and Na^{+} on bentonite colloid aggregation structures before and after dialysis, analyzing the mechanisms underlying ion valence effects on aggregation reversibility. These findings deepen our understanding of bentonite colloid environmental behavior and provide critical scientific evidence for safety assessment of high-level radioactive

waste repositories.

Experimental Methods

Materials and Instrumentation

Sodium-based bentonite (99% purity) was purchased from Shanlin Shiyu Mineral Products Co., Ltd. Analytical grade $CaCl_2$, NaCl, KCl, and $MgCl_2$ reagents were obtained from China Chemical Reagent Company. A NanoBrook Omni DLS instrument (Brookhaven, USA) measured hydrodynamic diameters using a 640 nm laser at 90° scattering angle and 25°C, with three consecutive 60-second measurements per sample. SAXS data were collected at beamline BL19U2 of the National Facility for Protein Science in Shanghai, using 0.103 nm X-rays at a sample-detector distance of 2678.6 mm, covering a scattering vector range of q = 0.06–4.26 nm^{-1} (q = $4\pi\sin$ /λ, where is half the scattering angle). BioXTAS RAW software processed experimental data, including 1D scattering curve conversion, direct beam normalization, and solvent background subtraction. Phase structures were characterized by X-ray diffraction (MiniFlex 600, Rigaku, Japan), morphology by transmission electron microscopy (Libra 200FE, Zeiss, Germany), and turbidity by a turbidity meter (TB200, Shanghai Bante Instruments).

Sample Preparation and Experimental Procedures

Ten grams of sodium bentonite powder was dispersed in 1000 mL ultrapure water (resistivity $\geq$ 18.2 M$\Omega \cdot$ cm), magnetically stirred at 200 rpm for 24 hours, and sonicated for 30 minutes. The resulting suspension was centrifuged at 6000 rpm for 30 minutes, and the supernatant was transferred to dialysis bags (molecular weight cutoff 8000–14000 kDa) for three days of dialysis in ultrapure water to remove impurity ions. Fifty milliliters of the prepared bentonite colloid solution was dried at 70°C for four days in three beakers, and the average mass concentration was determined gravimetrically. The stock solution was precisely diluted to obtain a series of known concentrations, and turbidity measurements established a standard calibration curve. The concentration of this batch of bentonite colloid was determined to be 1.8 mg/mL, which was diluted to 1.0 mg/mL for subsequent experiments.

In Beishan groundwater, typical Na^+ and Ca^{2+} concentrations range from 10–50 mmol/L and 1–6 mmol/L, respectively. High-concentration $CaCl_2$ and NaCl solutions were prepared and mixed with bentonite colloid solution at a 1:20 volume ratio, yielding final Ca^{2+} concentrations of approximately 1, 2, and 6 mmol/L, and Na^+ concentrations of approximately 10, 20, and 50 mmol/L. Samples were equilibrated for 72 hours before DLS and SAXS measurements.

For dialysis experiments, aggregated colloid solutions were centrifuged to obtain precipitates, which were resuspended in 10 mL ultrapure water and placed in dialysis bags (MWCO 8000–14000 kDa). Dialysis proceeded for 72 hours in

ultrapure water with solution changes every 12 hours until the final conductivity was <10 S/cm. Dialyzed samples were re-analyzed by DLS and SAXS to compare the reversibility of Ca^{2+}- and Na^{+}-induced aggregation.

Measurement Principles and Data Analysis

DLS measures hydrodynamic diameter by detecting intensity fluctuations of scattered light caused by Brownian motion of nanoparticles. For monodisperse systems, the intensity correlation function C(τ) follows the Siegert relation:

$$C(\tau) = 1 + \beta|g(\tau)|^2 = 1 + \beta e^{-2Dq^2\tau}$$

where g(τ) is the electric field correlation function, τ is delay time, q is the scattering vector magnitude (q = 4πnsin /λ, n is refractive index, is half the scattering angle), D is diffusion coefficient, and β is instrument efficiency factor. The hydrodynamic diameter follows the Stokes-Einstein relation: D = k T/(3π D), where k is Boltzmann' s constant, T is absolute temperature, and is solvent viscosity.

For polydisperse systems, the measured signal represents a weighted superposition of exponential decays from different particle sizes. The electric field correlation function is expressed as an integral:

$$g(\tau) = \int_0^\infty G(\Gamma)e^{-\Gamma\tau}d\Gamma$$

where Γ = Dq^2 and G(Γ) is the decay rate distribution function normalized by G(Γ)dΓ = 1. The CONTIN algorithm in NanoBrook software numerically inverts this equation to obtain G(Γ) and hydrodynamic diameter distribution. We use "equivalent hydrodynamic diameter D (nm)" to characterize the statistical average size of polydisperse bentonite colloids.

SAXS is a non-destructive technique that probes nanoscale structures through coherent scattering near the incident beam, arising from electron density fluctuations. The scattering intensity I(q) reveals particle size, morphology, and number density. For monodisperse, randomly oriented nanoparticles:

$$I(q) = NV^2\Delta\rho^2P(q)S(q)$$

where N is particle number density, V is particle volume, Δ is scattering contrast (scattering length density difference), P(q) is orientation-averaged form factor reflecting geometry, and S(q) is structure factor describing spatial arrangement. For dilute systems (<5% concentration), interparticle interactions are negligible (S(q) = 1).

For dilute solutions of randomly oriented platelet nanoparticles where lateral dimensions far exceed thickness, scattering intensity is:

$$I(q) = NV_{\text{cylinder}}^2 \Delta\rho_{\text{cylinder}}^2 \frac{2}{q^2} \exp\left(-\frac{q^2 L^2}{12}\right)$$

where V_{cylinder} is platelet volume, Δ _{cylinder} is contrast, L is platelet thickness, and R is lateral radius. When qR 1, I q^{-2}. Kratky plots (Iq^2 vs. q) reveal whether colloids possess ideal local lamellar structure. A horizontal line in the Kratky plot without diffraction peaks indicates monolayer structure.

If bentonite colloids form face-to-face stacked periodic structures, diffraction peaks appear in the high-q region of I-q curves, and interlayer spacing is calculated as d = 2π/q_{peak}. Edge-to-face aggregation increases low-q scattering intensity, deviating from I q^{-2}. Kratky plots clearly distinguish these aggregation states.

Results and Discussion

Microstructure of Bentonite Colloids

The XRD pattern of sodium bentonite shows main diffraction peaks belonging to montmorillonite, with a weak peak at 26.6° from quartz [Figure 1: see original paper]. The XRD pattern of powder dried from bentonite colloid solution exhibits only montmorillonite peaks; some peaks disappear due to preferred orientation during drying. The (001) plane spacing is 12.75 Å, consistent with literature values for sodium bentonite, confirming that our centrifugation-dialysis method yields high-purity bentonite colloids. In contrast, colloids prepared from GMZ bentonite typically contain cristobalite impurities.

SAXS data for bentonite colloid solution show a horizontal line in the Kratky plot (inset) over 0.06–0.6 nm^{-1}, indicating I q^{-2} [Figure 2: see original paper]. Fitting with Equation (4) shows excellent agreement, yielding a platelet thickness L = 1.06 ± 0.01 nm. Combined SAXS and TEM results confirm successful preparation of single-layer bentonite colloid suspensions [Figure 3: see original paper].

Effect of Ca^{2+} on Aggregation Reversibility

DLS measurements reveal significant aggregation of single-layer bentonite colloids across 1–6 mmol/L Ca^{2+} concentrations [Figure 4: see original paper]. After dialysis, aggregated particles partially disaggregate but size distributions do not fully recover. The equivalent hydrodynamic diameter D is 261 ± 11 nm in ultrapure water, increasing to (6.31 ± 1.08) × 10^3 nm, (6.51 ± 1.01) × 10^3 nm, and (6.53 ± 0.99) × 10^3 nm at 1, 2, and 6 mmol/L Ca^{2+}, respectively. After dialysis, D decreases to (1.29 ± 0.15) × 10^3 nm, (2.15 ± 0.32) × 10^3 nm,

and $(2.20 \pm 0.16) \times 10^3$ nm. DLS indicates that Ca^{2+}-induced bentonite colloid aggregates (secondary structures) are partially reversible at the micrometer scale.

SAXS data for Ca^{2+}-containing bentonite colloids show significantly increased I-q slope and a pronounced diffraction peak at q_{peak} = 3.38 nm^{-1} in the high-q region at 1 mmol/L Ca^{2+}, indicating face-to-face stacked periodic structures with d = 1.86 nm spacing [Figure 5: see original paper]. After dialysis, diffraction peak intensity and width remain unchanged, demonstrating that Ca^{2+}-induced lamellar stacking (primary structure) is irreversible. Kratky plots clearly show reduced upturn at low q after dialysis (arrows in FIGURE:5), suggesting disaggregation of larger secondary structures, consistent with DLS results.

Effect of Na^+ on Aggregation Reversibility

In Na^+-containing solutions, bentonite colloid hydrodynamic diameter distributions show significant aggregation at 10–50 mmol/L Na^+ that nearly completely reverses after dialysis [Figure 6: see original paper]. D increases to $(1.19 \pm 0.11) \times 10^3$ nm at 10 mmol/L Na^+ and ~ $(3.20 \pm 0.20) \times 10^3$ nm at 20 and 50 mmol/L Na^+. After dialysis, D decreases to 273 ± 13 nm, 291 ± 13 nm, and 289 ± 12 nm, closely approaching the initial value in ultrapure water.

SAXS data for Na^+-containing bentonite colloids show no diffraction peaks at 50 mmol/L Na^+, indicating absence of face-to-face stacking [Figure 7: see original paper]. Kratky plot upturn suggests edge-to-face aggregation forming loose "card-house" structures. After dialysis, the Kratky plot returns to a horizontal line in the low-q region (0.06–0.6 nm^{-1}), confirming disaggregation into monolayers. Both DLS and SAXS demonstrate that Na^+-induced aggregation is fully reversible.

Aggregation and Dispersion Mechanisms

Ca^{2+} (1–6 mmol/L) induces irreversible face-to-face periodic stacking (d = 1.86 nm) in bentonite colloids, forming stable primary aggregates [Figure 8: see original paper]. This phenomenon is understood through two mechanisms. First, classical DLVO theory predicts that divalent cations (Ca^{2+}, Mg^{2+}) are far more effective aggregating agents than monovalent cations (Na^+, K^+). Ca^{2+} addition substantially increases ionic strength, reducing Debye screening length, compressing electric double layers, and weakening electrostatic repulsion. Second, Ca^{2+}' s high charge density creates a tightly bound positive ion layer near bentonite surfaces, reducing effective negative surface charge and potentially causing local charge reversal. Ca^{2+} likely forms "bridges" between adjacent surfaces, generating short-range attraction that overcomes interlayer repulsion and induces irreversible face-to-face aggregation. This mechanism also explains why calcium-based bentonite poorly disperses into stable colloids. The observed d-spacing of 1.86 nm matches that of calcium-based bentonite after swelling and

corresponds to the sum of monolayer thickness (~1 nm) and hydrated Ca^{2+} diameter (0.8–0.9 nm), supporting this bridging mechanism.

In contrast, Na^+ at 10–50 mmol/L induces fully reversible, loose edge-to-face aggregation [Figure 7: see original paper]. Within this concentration range, Na^+ compresses electric double layers, promoting electrostatic attraction between positively charged edges and negatively charged basal surfaces to form "card-house" structures. Dialysis reduces Na^+ concentration, increasing Debye length and restoring electrostatic repulsion, causing "card-house" disaggregation into monolayers. In mixed Ca^{2+}-Na^+ systems, scattering features match those of Ca^{2+}-bentonite systems [Figure 8: see original paper], indicating Ca^{2+}-dominated aggregation behavior. Xu et al.' s column studies showed that while both Ca^{2+} and Na^+ cause bentonite colloid aggregation and retention in quartz porous media, only Na^+-induced aggregates can be eluted with pure water. Our results explain this microscopically: Ca^{2+} forms stable periodic structures that remain retained and resist elution and disaggregation. The aggregation and dispersion processes are schematically illustrated in [Figure 9: see original paper].

Implications for High-Level Radioactive Waste Geological Disposal

DLS analyzes size changes from hundreds of nanometers to micrometers, while SAXS excels at resolving local aggregation structures from 0.5 to 200 nm. Combining these techniques enables characterization of both primary and secondary bentonite colloid structures across scales. Synchrotron SAXS data particularly reveal microscopic and mesoscopic aggregation behavior, providing powerful technical support for repository safety assessment.

Beishan groundwater is primarily $Cl \cdot SO_4$-Na and $SO_4 \cdot Cl$-Na type ($7.5 < pH < 8.5$), containing considerable K^+ (0.1–1 mmol/L) and Mg^{2+} (0.5–3 mmol/L) in addition to Ca^{2+} and Na^+. For example, deep groundwater from borehole BS06 contains 6.24 mmol/L Ca^{2+}, 30.22 mmol/L Na^+, 0.85 mmol/L Mg^{2+}, and 0.17 mmol/L K^+. SAXS data for bentonite colloids in 2× and 10× diluted BS06 groundwater [Figure 10: see original paper] suggest that divalent cations (Ca^{2+}, Mg^{2+}) induce face-to-face stacking. This stable aggregation likely inhibits radionuclide migration near the repository through deposition, filtration, and clogging mechanisms.

Conclusions

This study combined DLS and SAXS to investigate Ca^{2+} and Na^+ effects on bentonite colloid aggregation structures and reversibility in Beishan groundwater environments, elucidating aggregation mechanisms and advancing understanding of bentonite colloid environmental behavior. The main conclusions are:

1. Ca^{2+} induces stable face-to-face stacked periodic structures (d = 1.86 nm) that are irreversible; dialysis partially disaggregates micrometer-scale secondary structures while periodic structures remain intact. Na^+ induces

reversible "card-house" structures that completely disaggregate after dialysis. In mixed systems, Ca^{2+} dominates aggregation behavior.

2. Ca^{2+} likely bridges adjacent surfaces via short-range attraction, overcoming electrostatic repulsion to cause irreversible aggregation. Na^{+} compresses electric double layers to form loose "card-house" structures that disaggregate when Debye length increases after dialysis.

3. Beishan groundwater contains substantial alkaline earth cations (Ca^{2+}, Mg^{2+}) that maintain bentonite colloids in irreversible aggregated (sedimented) states, potentially inhibiting bentonite colloid-radionuclide migration and enhancing repository safety.

4. Synchrotron SAXS is a powerful non-destructive technique for analyzing weakly scattering colloidal systems, with broad prospects for studying bentonite colloid formation and migration mechanisms.

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Author Contributions

DU Jin and ZHU Yi contributed equally: conducted experiments, performed data analysis, and wrote the manuscript. LI Jiebiao contributed resources and reviewed the manuscript. TIAN Qian designed experiments, provided technical support, and reviewed the manuscript. LIU Chunli managed the project and reviewed the manuscript.

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Note: Figure translations are in progress. See original paper for figures.