Time-resolved effects of electrolyte chemistry on kaolinite consistency: toward a kinetic, DLVO-informed interpretation

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1 Introduction

Electrolyte chemistry exerts a strong influence on the mechanical behaviour of clay-rich soils, governing processes such as flocculation, compressibility, undrained shear strength, seepage and long-term settlement. These effects are particularly important in geotechnical settings where pore-water chemistry evolves over time, such as coastal environments undergoing salinisation, landfills, embankment and engineered barriers exposed to leachates, and soft soils affected by industrial contamination or groundwater recharge. Despite this, most models assume static chemical conditions and equilibrium microfabrics. Re-interpreting classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory to account for time-dependent ion–clay interactions is therefore necessary for more realistic prediction of soil behaviour under chemically dynamic conditions. This study addresses this need by examining how concentration, valency and exposure time jointly affect kaolinite consistency.

Kaolinite, a 1:1 phyllosilicate clay, exhibits low swelling potential and minimal isomorphic substitution, resulting in low cation exchange capacity (CEC) [1]. These characteristics challenge the applicability of classical DLVO theory, which predicts that increasing ionic concentration and valency compresses the diffuse-double-layer, reducing electrostatic repulsion and promoting flocculation [2, 3]. While this framework is widely validated for smectite clays [4], its relevance to kaolinite remains debated due to anisotropic charge distribution and edge-controlled interactions [5].

DLVO theory expresses double-layer thickness (Debye length, κ^{-1}) as:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon k_B T}{2ne^2v^2}} \tag{1}$$

Where ε is permittivity, k_B is Boltzmann's constant, T is temperature, n is the number concentration of ions (ions m^{-3}), e is elementary charge, and v is ionic valency. This relationship shows that increasing ionic concentration and valency reduces κ^{-1}, compressing the diffuse-layer and promoting particle aggregation or flocculation. In electrolyte solutions containing multiple ionic species, this relationship is commonly expressed in terms of ionic strength, which explicitly accounts for both ion concentration and valency [3].

For multivalent electrolytes, comparisons at equal salt molarity do not correspond to equal electrostatic conditions, as diffuse-double-layer compression scales with ionic strength, which incorporates both ion concentration and valency squared. Accordingly, apparent valency effects may reflect combined influences of ionic strength and ion-specific surface interactions.

Recent studies confirm that electrolyte chemistry influences kaolinite behaviour, with higher-valence cations such as Al^{3+} exerting stronger charge neutralisation and hydration effects than monovalent ions [6]. However, most investigations adopt a static equilibrium perspective, overlooking the role of exposure time in microfabric evolution, a gap noted by [7]. This omission is significant because ion – clay interactions are not instantaneous; they may involve gradual processes such as cation bridging and edge – face networking.

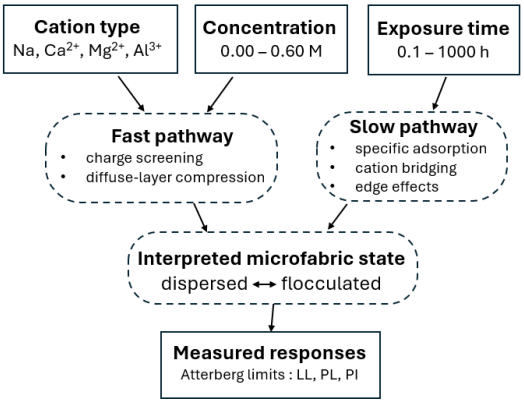

Figure 1. Conceptual framework for the time-resolved influence of electrolyte chemistry on kaolinite consistency, linking cation type, concentration, and exposure time to inferred microfabric evolution and measured Atterberg limits (LL, PL, PI).

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Figure 1 summarises a conceptual framework linking electrolyte chemistry and exposure time to changes in kaolinite consistency. Variations in ionic concentration and cation valency influence fast electrostatic processes, such as charge screening and diffuse-double-layer compression, while longer exposure times permit slower, ion-specific mechanisms including adsorption, cation bridging, and edge – face interactions. Together, these processes contribute to an inferred evolution of clay microfabric along a dispersed–flocculated continuum.

As interparticle associations become stronger, the soil requires less water to reach a given consistency state, leading to overall reductions in liquid limit (LL) and plasticity index (PI). These Atterberg limits therefore act as measurable macroscale proxies for chemically and temporally driven microfabric evolution. Over longer exposure times, the extent and reversibility of these changes depend on electrolyte type and concentration, with moderate concentrations permitting partial reversibility and higher concentrations promoting sustained fabric alteration.

This study addresses these gaps by examining the combined effects of electrolyte concentration, ionic valency, and exposure time on the Atterberg limits of Speswhite kaolin. By integrating chemical and kinetic factors, we aim to develop a time-resolved, DLVO-informed interpretation of kaolinite consistency that links electrolyte chemistry with exposure time, providing insights for geotechnical modelling and engineered barrier design under chemically dynamic conditions.

2 Materials and methods

Speswhite kaolin, a mono-mineral clay with low organic content and consistent mineralogy, was used for all tests; its key properties include a specific gravity of 2.60, a pH of approximately 5.5, and a surface area of 14 m²/g. Electrolyte solutions were prepared using analytical-grade NaCl, $MgCl_2$, $CaCl_2$ and $AlCl_3$ to represent mono-, di- and trivalent cations, with concentrations ranging from 0.00 to 0.60 M in reverse osmosis water to minimise background ionic interference. Clay pastes with a water content of approximately 40 % were exposed to electrolyte solutions and sealed at 20 ± 1 °C for between 0.1 and 1000 h prior to testing, to capture both short- and long-term clay – electrolyte interactions. Liquid limit measurements were repeated until two consecutive cone penetrations differed by less than 0.5 mm, while plastic limit values were obtained from duplicate tests within 0.5 % water-content difference; mean values were used in subsequent analysis, and repeatability fell within expected Atterberg-limit tolerances. The plasticity index was computed as the difference between the liquid and plastic limits. Relationships between LL/PI and electrolyte concentration, ionic valency and exposure time were evaluated using regression and Spearman rank correlation, with log-linear slopes quantifying ageing rates per decade of time.

Electrolyte concentrations are reported in terms of salt molarity for experimental control and reproducibility; however, differences in ionic strength associated with cation valency are explicitly considered in the interpretation of results. Porewater pH was measured before and after testing. While NaCl, $CaCl_2$, and $MgCl_2$ systems remained near-neutral to mildly acidic, $AlCl_3$ solutions exhibited consistently low pH values (Approx. 2.4 – 3.8), reflecting Aluminium hydrolysis and speciation during exposure.

3 Results and discussion

3.1 Effect of electrolyte concentration and valency

For a given electrolyte type and concentration, plastic limit (PL) values exhibited limited systematic variation with exposure time; consequently, concentration-dependent changes in plasticity are reflected primarily through variations in liquid limit (LL) and plasticity index (PI). LL and PI decreased systematically with increasing electrolyte concentration for all salts tested (Figure 2).

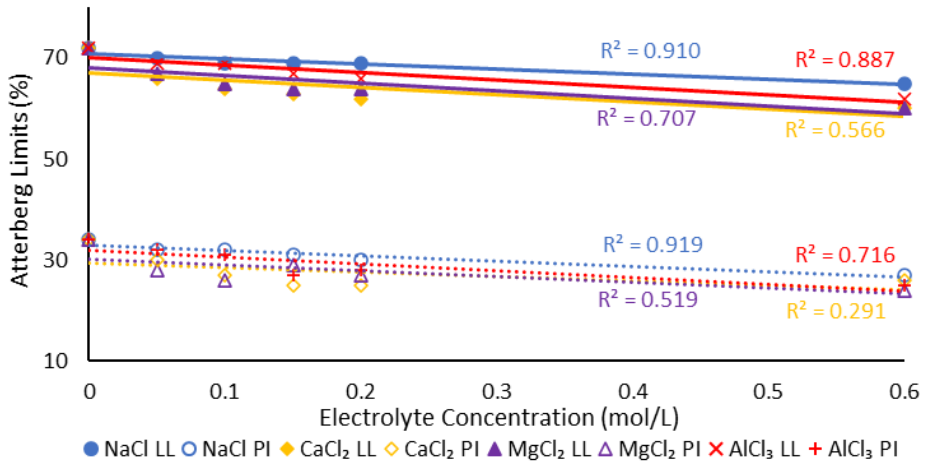

Figure 2. Variation of liquid limit (LL) and plasticity index (PI) of Speswhite kaolin with electrolyte concentration for NaCl, $CaCl_2$, $MgCl_2$, and $AlCl_3$ solutions after 0.1h exposure time.

While multivalent cations produced larger reductions overall than Na^+, the concentration response did not exhibit a consistent monotonic ranking with cation valency, with Ca^{2+} and Mg^{2+} often reducing LL and PI to a similar or greater extent than Al^{3+} at equal molarity [2, 3]. For example, $AlCl_3$ caused rapid PI decline at low molarity; however, comparable or larger reductions were observed for $CaCl_2$ and $MgCl_2$ at similar concentrations, highlighting the combined roles of ionic strength, hydration, and ion-specific surface interactions, while NaCl exhibited only modest changes. Regression analysis confirmed strong concentration dependence for LL ($R^2 > 0.88$ for NaCl and $AlCl_3$), whereas PI correlations were weaker for divalent salts, suggesting additional factors such as hydration shell size and edge-site interactions [5]. Measured post-exposure pH values indicate that $AlCl_3$ systems remained strongly acidic (pH 2.4 – 3.8), implying significant Al hydrolysis and pH-dependent modification of kaolinite edge-charge. Consequently, the pronounced effects observed for $AlCl_3$ likely reflect a combination of high ionic strength, Al speciation, and pH-mediated edge–face interactions, rather than diffuse-double-layer compression alone.

A noticeable gap exists between 0.20 M and 0.60 M for all salts, where LL and PI change more abruptly than in adjacent concentration ranges. Additional experiments at intermediate concentrations (0.30 – 0.50 M) are currently being conducted to clarify whether this transition reflects a threshold compression of the diffuse-double-layer or a change in cation – surface interaction mechanisms.

3.2 Time-resolved behaviour

Exposure time produced clear kinetic effects on kaolinite consistency that complemented the static influence of electrolyte concentration and valency. At 0.10 M (Figures 3a and 3c), all electrolytes exhibited non-monotonic, time-dependent behaviour. Ca^{2+} and Mg^{2+} showed small positive ageing in ΔLL and ΔPI, consistent with gradual cation bridging and edge – face structuration, while Na^+ exhibited modest fluctuations rather than strictly stable behaviour over time [5, 7]. Al^{3+} exhibited minimal drift, reflecting the limited ability of its strongly hydrated ions to interact closely with clay surfaces at moderate concentration [6].

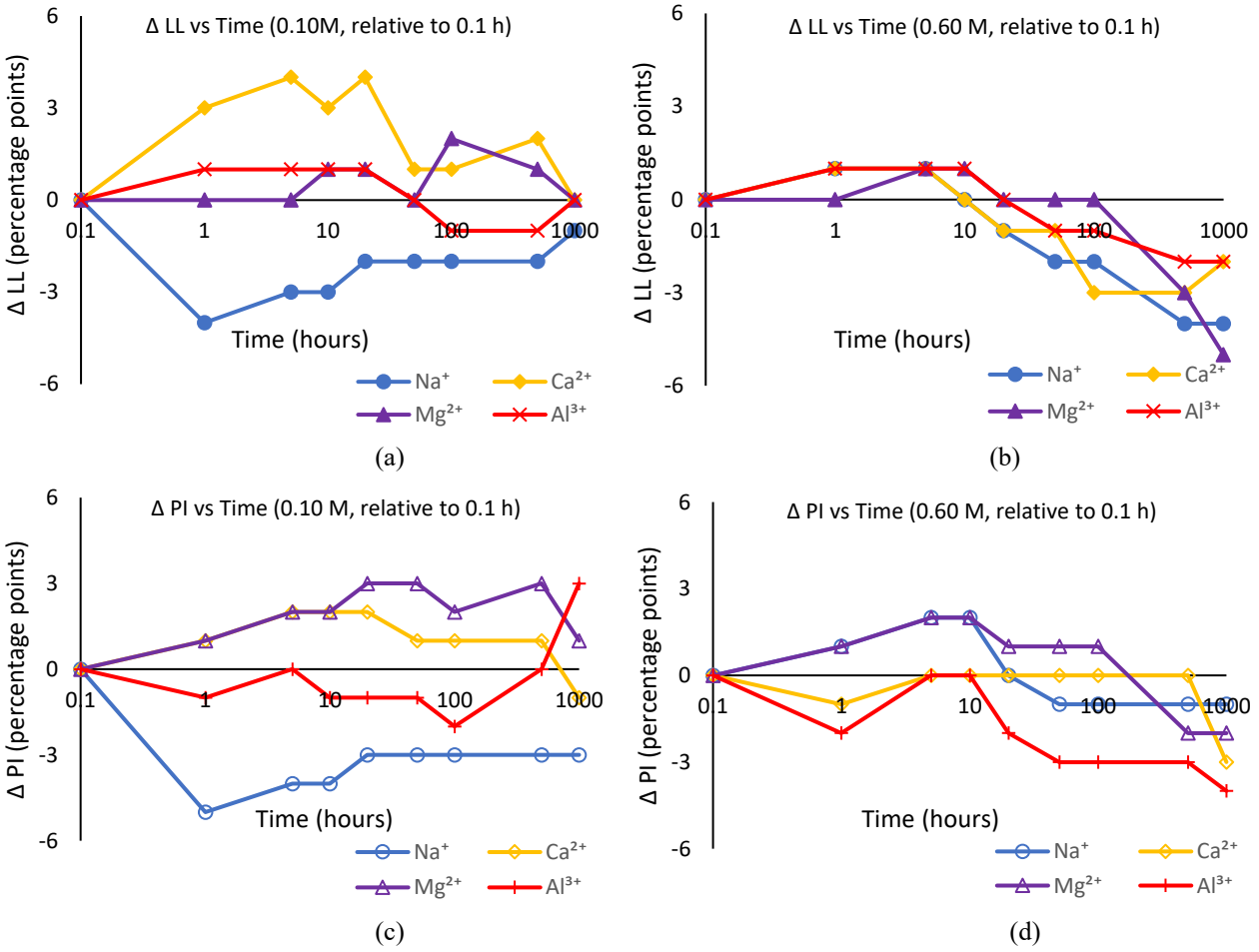

Figure 3. Time-resolved changes in liquid limit (ΔLL) (a & b) and plasticity index (ΔPI) (c & d) for kaolinite exposed to Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+} solutions at two concentrations: (a & c) 0.10 M and (b & d) 0.60 M.

Although interparticle forces, zeta potential, and clay microfabric were not measured directly, the systematic and time-dependent evolution of the Atterberg limits provides macroscale evidence consistent with DLVO-type mechanisms acting under non-equilibrium chemical conditions.

Together, Figures 3a – d show that moderate electrolyte concentrations may permit slow, reversible microfabric development, whereas high concentrations impose sustained, time-dependent consolidation, supporting a kinetic, DLVO-informed interpretation relevant for chemically dynamic environments.

These results reinforce the conceptual framework in Figure 1, demonstrating that the chemical controls on double-layer compression and flocculation extend beyond equilibrium states and can be tracked macroscopically through the time-dependent evolution of the Atterberg limits.

4 Conclusion

The results indicate that kaolinite consistency depends on both electrolyte chemistry and exposure duration, and they support a time-dependent DLVO-informed interpretation rather than a purely static equilibrium view. Increasing electrolyte concentration and associated ionic strength promote diffuse-double-layer compression, contributing to reductions in liquid limit (LL) and plasticity index (PI) in a manner broadly consistent with DLVO expectations. Time-resolved analyses reveal that exposure duration exerts a measurable kinetic effect: high electrolyte concentration (e.g., 0.60 M NaCl, $CaCl_2$, $AlCl_3$) produces monotonic declines in LL at log-linear rates up to −1.31 percentage points per decade, whereas mid-range concentrations of multivalent cations exhibit slight positive ageing, suggesting gradual cation bridging and edge–face networking. These findings indicate that kaolinite microfabric evolves not only under equilibrium chemical conditions but also through time-dependent processes. Incorporating these effects into predictive models is essential for geotechnical applications involving chemically dynamic environments, such as engineered barriers and soft soil behaviour in saline or contaminated systems.

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Author contributions are as follows: Kabiru Adebayo was responsible for funding acquisition, conceptualisation, writing – original draft, methodology, experimentation, result analysis, visualisation, and validation. Ken Vinck contributed to conceptualisation, writing – review and editing, supervision, project administration, resources, and validation. Angela Casarella contributed to conceptualisation, writing – review and editing, supervision, methodology and validation. Catherine O'Sullivan contributed to conceptualisation, writing – review and editing, supervision, project administration, resources, and validation. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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