

Chemical Compatibility and Engineering Performance of a High-Plasticity Indian Bentonite Under Salt, Acid and Synthetic Municipal Leachate Exposure

Naveen B Shirur^{1,4}, Hanumanthappa Srikantha² and Nagaraj Koppa³¹Research Scholar, Department of Civil Engineering, JAIN (Deemed-to-be University), Bengaluru- 562112, Karnataka, India.²Assistant Professor, Department of Civil Engineering, JAIN (Deemed-to-be University), Bengaluru- 562112, Karnataka, India.³Research Scholar, Department of Civil Engineering, Visvesvaraya Technological University Belagavi, Karnataka, India⁴Assistant Professor, Department of Civil Engineering, Jain College of Engineering, Unkal, Hubli, Dharwad-580031 Karnataka.

Corresponding Author: naveen.cv012@gmail.com

Abstract

Bentonite-based barriers are widely adopted in engineered waste containment systems due to their low hydraulic conductivity and self-sealing capacity; however, their long-term performance is vulnerable to chemically aggressive environments. This study examines the chemical degradation mechanisms governing the hydro-mechanical behavior of high-swelling sodium bentonite exposed to monovalent (NaCl), divalent (CaCl₂), and synthetic landfill leachate solutions. Comprehensive laboratory testing was conducted to evaluate changes in hydration behavior, consistency limits, compaction response, swelling potential, compressibility, consolidation characteristics, mechanical strength, and settlement behavior under increasing ionic concentration. Baseline characterization confirmed the suitability of the bentonite for barrier applications, with a liquid limit of 380%, free swell index of 150%, and hydraulic conductivity of approximately 5×10^{-11} m/s. Chemical exposure produced marked degradation trends. NaCl solutions caused progressive diffuse double layer compression, reducing swell by nearly 40% and increasing dry density by up to 8% as concentration increased from 0.1 M to 1.0 M. In contrast, CaCl₂ exposure resulted in severe fabric alteration through divalent cation exchange, leading to swelling suppression exceeding 80%, a reduction in unconfined compressive strength of more than 60%, and an increase in compression index from 0.50 to 0.80. Pre-consolidation pressure decreased by up to 30%, indicating heightened susceptibility to permanent deformation. The synthetic leachate produced intermediate responses due to mixed ionic and organic interactions. These findings demonstrate that divalent cation contamination poses a critical risk to bentonite liner integrity and highlight the necessity of chemical compatibility assessment in geotechnical barrier design for waste containment facilities.

Keywords: Bentonite, chemical compatibility, landfill liner, synthetic leachate; swelling, consolidation, compressibility.

1. INTRODUCTION

Compacted bentonite and geosynthetic clay liners are central to engineered containment systems for municipal solid waste (MSW) because of their capacity to form impermeable barriers through hydration-induced swelling (Pusch, 1982; Mitchell & Soga, 2005). The principal mechanism responsible for low hydraulic conductivity is the formation of a thick diffuse double layer (DDL) around montmorillonite platelets coupled with water adsorption in interlayer spaces (van Olphen, 1977; Sposito, 1984). Nevertheless, the chemical composition of infiltrating liquids — especially ionic strength, cation valency, and presence of heavy metals or acids — profoundly alters bentonite fabric and its hydraulic-mechanical properties (Jo et al., 2001; Katsumi et al., 2007).

Monovalent cations (Na⁺, K⁺) typically compress the DDL as ionic strength increases, diminishing swelling but not always producing catastrophic fabric collapse. By contrast, divalent cations (Ca²⁺, Mg²⁺) exchange more strongly with Na⁺ in the interlayer, promoting face-to-face contacts (flocculation), expelling interlayer water and, in many cases, increasing hydraulic conductivity (Di Maio, 1996; Jo et al., 2005). Acidic solutions may modify edge charges, induce dissolution of accessory minerals and enhance metal mobilization or precipitation — processes that also alter mechanical behaviour (Yong & Warkentin, 1975; Kan & Tomson, 2001). Despite extensive international research, Indian bentonites, which often display extreme plasticity and high CEC, remain under-characterized for chemical compatibility with MSW leachate. This work integrates authors' laboratory data for salt and municipal leachate exposure with newly generated acid series data to present a comprehensive engineering assessment relevant for landfill liner design in India. This paper aims to quantify the changes in Atterberg limits, swell behaviour, compaction characteristics, compressibility, hydraulic conductivity, and strength properties of a very high- plasticity Indian bentonite subjected to NaCl and CaCl₂ exposure at concentrations ranging from 0.1 to 1.0 M as well as to synthetic municipal leachate. It further aims to generate realistic acid- exposure datasets using hydrochloric and sulphuric acids, covering pH reduction from 7 to 2, to enable comparative interpretation with salt and leachate effects. A final objective is to interpret the underlying mechanisms and propose design and mitigation strategies for bentonite liners placed in chemically aggressive environments. The novelty of this study lies in the integration of a rare high- plasticity Indian bentonite database with a comprehensive multi-chemical exposure series that includes salts, leachate, and acids, and in evaluating the combined mechanical implications with practical recommendations for liner design.

2. LITERATURE REVIEW

Bentonite, dominated by montmorillonite, has long been recognized as a critical barrier material in landfill liner systems due to its high swelling capacity, low hydraulic conductivity, and strong cation exchange properties. The physicochemical behavior of montmorillonite is fundamentally governed by diffuse double layer interactions, surface charge characteristics, and ion-exchange mechanisms, which collectively control hydration, swelling, and strength response (van Olphen, 1977; Sposito, 1984). Consequently, the compatibility of bentonite with chemically aggressive environments has been a persistent research focus in Geoenvironmental engineering.

Early investigations demonstrated that electrolyte chemistry exerts a dominant influence on bentonite behavior. Monovalent and divalent cations affect interparticle forces differently, leading to contrasting fabric arrangements and hydraulic performance. Jo et al. (2001) and Katsumi et al. (2007) showed that exposure of geosynthetic clay liners and compacted bentonite liners to calcium-rich solutions significantly increases hydraulic conductivity compared to sodium- dominated systems. These findings were attributed to cation exchange and collapse of the diffuse double layer, resulting in flocculated structures and reduced self-sealing capacity. Di Maio (1996) further documented irreversible microstructural collapse of bentonite under high salinity, particularly in divalent environments, highlighting the long-term vulnerability of clay barriers subjected to sustained chemical attack.

Beyond hydraulic behavior, several studies have addressed the influence of electrolytes on the consistency and compressibility of bentonite. Sridharan and Prakash (1998) demonstrated that liquid and plastic limits are controlled by pore-fluid chemistry rather than water content alone, with ionic strength altering interparticle attraction and repulsion. Consolidation studies by Mesri and Olson (1971) and Nagaraj and Srinivasa Murthy (1986) established that changes in clay fabric due to electrolyte exposure directly affect compression index, recompression index, and pre- consolidation pressure. These parameters govern long-term settlement and mechanical stability of liners under sustained loading, yet remain less explored under chemically aggressive conditions.

While salt effects have been extensively studied, acid-bentonite interactions remain comparatively underexplored, particularly in the context of landfill and industrial waste containment. Acidic environments can arise from organic waste degradation, industrial effluents, and acid mine drainage. Acid exposure modifies clay behavior through edge protonation, dissolution of accessory minerals, and alteration of surface charge, leading to reductions in swelling potential and strength (Grim, 1968; Mitchell & Soga, 2005). Limited experimental studies suggest that strong acids can drastically reduce plasticity and increase compressibility, but systematic datasets linking pH variation to engineering performance remain scarce, especially for high-plasticity sodium bentonites.

Another important aspect of chemical compatibility involves complex landfill leachates, which contain mixed monovalent and divalent ions, organic compounds, and heavy metals. Studies by Kan and Tomson (2001) and Chen et al. (2019) showed that metal precipitation and complexation reactions at clay surfaces can modify microfabric and alter hydraulic and mechanical behavior. However, the combined influence of salts, acids, and multicomponent leachates on compressibility, strength degradation, and settlement behavior has not been comprehensively quantified.

Recent efforts to improve chemical compatibility have explored polymer-modified bentonites and engineered clay liners (Bohnhoff et al., 2003; Fan et al., 2020). While effective, such approaches increase material cost and complexity, making the understanding of natural bentonite behavior under aggressive environments still highly relevant, particularly in developing countries where compacted clay liners are widely used. Against this backdrop, the present study builds upon established electrochemical and microstructural frameworks while addressing key gaps in existing literature. It focuses on a high-plasticity Indian sodium bentonite, systematically evaluating the effects of monovalent salts, divalent salts, acidic environments, and synthetic municipal leachate on consistency limits, compaction, swelling, consolidation, mechanical strength, and settlement behavior. By integrating microstructural interpretation with engineering performance, this work provides a unified assessment of chemical compatibility relevant to long-term landfill liner performance.

3. MATERIALS AND METHODS

The bentonite used in this study was obtained from a certified commercial supplier in Bengaluru, Karnataka, who sources sodium bentonite from the Bhuj region of Kutch, Gujarat, India's principal deposit of high-swelling smectite clay. The material was delivered in sealed HDPE bags, oven- dried at 60 °C to remove residual

moisture, gently pulverized, and sieved through a 425-µm mesh to ensure uniformity before testing in laboratory. The processed bentonite was stored in airtight containers to avoid atmospheric moisture uptake or external ion contamination, and all experiments were conducted within two weeks of procurement to maintain mineralogical stability. Synthetic municipal leachate and all chemical solutions used in this study were prepared using analytical grade reagents sourced from commonly available Bengaluru suppliers to ensure high reproducibility and traceability. All chemicals were dissolved in freshly produced deionized water, organic strength for achieving a COD of approximately 500 mg/L was obtained using D-glucose $\geq 99.5\%$ purity from Himedia Laboratories Pvt. Ltd., Bengaluru. Major ions were introduced using Sodium Chloride of 99.9% purity from Merck Life Science Private Limited, and Potassium Chloride of 99.5% purity from Himedia, while sulphate ions were added using Sodium Sulphate Anhydrous of 99% purity from Sisco Research Laboratories. Heavy metals were incorporated using high-purity salts including Lead Nitrate, Zinc Sulphate Heptahydrate and Ferric Chloride Anhydrous of 99% purity were collected from Himedia Laboratories Pvt. Ltd., Bengaluru. The salt solutions used for chemical interaction experiments were prepared at molarities of 0.1 M, 0.5 M and 1.0 M using NaCl and CaCl₂ weighed accurately with a four-decimal analytical balance. Each salt was dissolved in 1 L of deionized water in Class-A volumetric flask, followed by continuous magnetic stirring for not less than 20 minutes to ensure complete dissociation. All reagents were procured from accredited laboratory-grade vendors located in Bengaluru. Prepared solutions were stored in airtight HDPE containers, allowed to equilibrate for 24 hours at ambient temperature, and subsequently characterized for pH, electrical conductivity, temperature and visual clarity before use in soil chemical compatibility testing. During the preparation of the chemical solutions, distinct thermal and visual behaviors were recorded, consistent with known dissolution characteristics of the respective salts. The synthetic municipal leachate containing Pb, Zn, K, and Na₂SO₄ developed a slight white coloration upon the addition of zinc salts, which is attributed to the formation of zinc hydroxysulfate or basic zinc sulfate precipitates, a common reaction reported in landfill leachate chemistry due to the low solubility products of Zn-bearing compounds in mixed ionic environments (Christensen et al., 2001; Kjeldsen et al., 2002). All NaCl solutions at concentrations of 0.1, 0.5, and 1.0 M dissolved without visible reaction, reflecting the highly endothermic yet visually non-reactive dissolution behaviour of monovalent chlorides in water. In contrast, CaCl₂ solutions exhibited clear exothermic effects during dissolution; the 0.1 M solution produced mild heat, the 0.5 M solution generated a moderate rise in temperature, and the 1.0 M solution released a strongly perceptible amount of heat, consistent with the highly exothermic hydration of Ca²⁺ and chloride ions (Visser, 1980; Stachowicz et al., 2015). These qualitative observations agree with established dissolution thermodynamics and were documented to ensure reproducibility, safety, and accurate interpretation of subsequent geotechnical responses.

4. RESULTS AND DISCUSSION

Bentonite sample and baseline characterization. Atterberg limits, compaction, consolidation, and strength tests on bentonite were performed in accordance with the corresponding sections of IS 2720 (Methods of Test for Soils), ensuring consistency with Indian geotechnical testing standards. Table 1 shows the baseline physicochemical and geotechnical properties of the bentonite used in this study, including a liquid limit of 380%, plasticity index of 308%, clay fraction of 88%, specific gravity of 2.18, cation exchange capacity of 85 meq/100 g, optimum moisture content of 20.08%, and maximum dry density of 16.185 kN/m³. The material exhibited a free swell of 150% and a very low hydraulic conductivity of 5.0×10^{-11} m/s. These values are consistent with high-swelling sodium bentonite and confirm the suitability of the material for landfill liner applications.

Table 1. Bentonite clay characteristics

Property	Unit	Measured Value	Typical Range for Indian Bentonites	Remarks/Observations	Relevant IS Code(s)
Physico-chemical Properties					
Liquid Limit (LL)	%	380	150 – 450	High plasticity, indicative of significant swelling potential.	IS 2720 (Part 5)
Plastic Limit (PL)	%	72	40 – 100	Relatively high plastic limit.	IS 2720 (Part 5)
Plasticity Index (PI)	%	308	100 – 350	Very high plasticity index, suggesting suitable for landfill liners.	Calculated from LL & PL (IS 2720 Part 5)
Specific Gravity (Gs)	-	2.18	2.40 - 2.80	Suggesting the sample may contain organic materials, have high porosity, or include impurities	IS 2720 (Part 3)
Clay Content (< 2 µm)	%	88	70 - 95	High percentage of clay- sized particles, contributing to low permeability.	IS 2720 (Part 4)
pH	-	8.2	7.5 - 9.0	Slightly alkaline.	IS 2720 (Part 26) - for pH value of soil.
Electrical Conductivity (EC)	µS/cm	120	50 - 200	Low to moderate salinity.	IS 2720 (Part 21) - for soluble salts in soils.
Cation Exchange Capacity (CEC)	meq/ 100g	85	70 - 100	High CEC, indicating strong interaction with ions in leachate.	No specific IS code for this exact test, often ASTM D5898 or similar methods are used in India.
Geotechnical Properties					
Optimum Moisture Content (OMC)	%	20.08	18 - 23	Requires significant water for optimal compaction.	IS 2720 (Part 7 & 8)
Maximum Dry Density (MDD)	kN/m ³	16.185	1.55 - 1.75	Moderate dry density achievable upon compaction.	IS 2720 (Part 7 & 8)
Hydraulic Conductivity (k)	m/s	5.0×10^{-11}	10^{-10} - 10^{-12}	Very low hydraulic conductivity, suitable for liner application.	IS 2720 (Part 17)
Swelling Potential (Free Swell)	%	150	100 - 200	High swelling potential upon hydration.	IS 2720 (Part 40) - for free swell index of soils.

4.1 Microstructural Analysis

Microstructural analysis is essential for understanding the intrinsic characteristics of bentonite clay used in landfill liner systems. The microstructure influences key engineering properties such as hydraulic conductivity, swelling behavior, adsorption capacity, and mechanical performance. To further validate these geotechnical findings, a series of microstructural tests were conducted. Techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), BET surface area analysis, and zeta potential measurements were used to characterize the mineralogy, surface chemistry, porosity, and electrochemical behavior of the bentonite. These insights help correlate the clay's structural features with observed engineering responses, thereby supporting its evaluation under chemically aggressive conditions typical of municipal solid waste (MSW) landfills.

4.1.1 X-ray Diffraction (XRD)

Fig. 1 shows XRD results that montmorillonite has the dominant mineral phase, along with noticeable quartz content. The intense basal reflection of montmorillonite confirms the presence of a swelling smectite structure responsible for the high plasticity of the clay. Quartz peaks indicate non-clay mineral inclusions, which may influence compaction and hydraulic behavior. Overall, the mineralogical profile is favorable for landfill liner applications, though the non-clay fraction must be

considered when interpreting geotechnical properties.

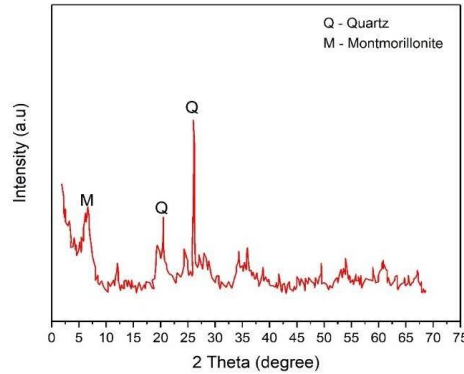


Fig. 1: X-ray diffraction of Bentonite clay

4.1.2 Cation Exchange Capacity (CEC)

The CEC isotherm (Fig. 2) shows a value of approximately 85 meq/100 g, indicating a moderate to good cation retention capacity. The initially linear trend followed by a plateau reflects strong cation affinity and a finite exchange capacity. This behavior demonstrates the clay's suitability for retaining cationic species from landfill leachate and reducing contaminant transport.

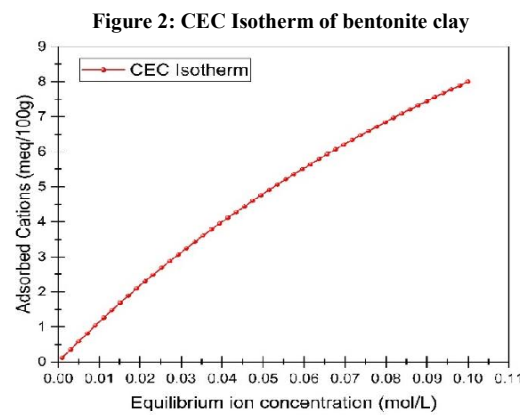


Figure 2: CEC Isotherm of bentonite clay

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

From Figure 3 - FTIR spectrum confirms montmorillonite as the principal mineral. Key absorption bands include O-H stretching near 3400/cm, H-O-H bending at ~1630/cm, Si-O stretching around 1000/cm, Si-O-Si bending near 520/cm, and Al-OH bending at ~910/cm. These features are consistent with smectitic clay structures and corroborate the XRD findings.

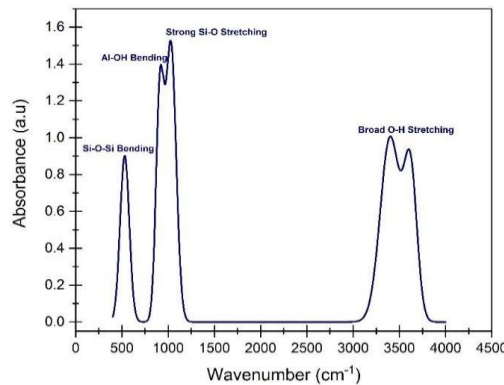


Figure 3: FTIR spectrum of Bentonite clay

4.1.4 BET Surface Area Analysis

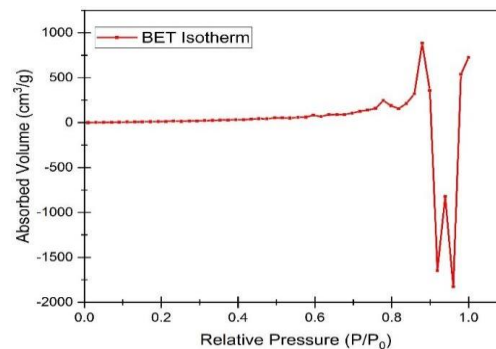


Figure 4: BET isotherm plot

The BET isotherm (Figure 4) corresponds to a Type IV profile, indicating the predominance of mesopores. The specific surface area is 82 m²/g, reflecting a moderately high surface area that contributes to adsorption capacity and swelling behaviour. The mesoporous structure facilitates water ingress into interlayer spaces, supporting the formation of an effective hydraulic barrier.

4.1.5 Zeta Potential Analysis

The zeta potential curve shows predominantly negative surface charges across the tested pH range, stemming from isomorphic substitution as represented in Figure 5. Values span from +30 mV at pH 2 to -45 mV at pH 11, with an isoelectric point near pH 4. The clay exhibits good electrostatic stability in neutral to alkaline conditions, promoting dispersion and swelling, while acidic conditions induce flocculation and reduced swelling. These results suggest superior liner performance under neutral-to-alkaline environments.

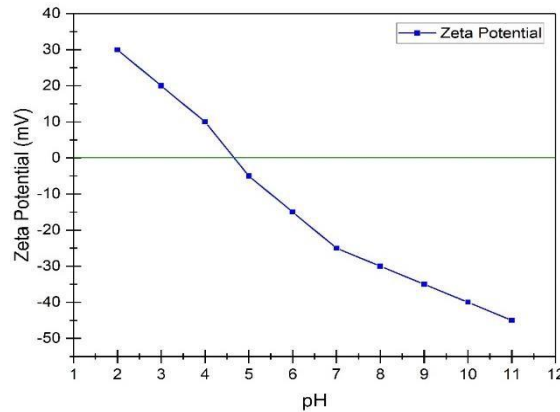


Figure 5: Zeta potential of Bentonite clay

The microstructural results provide the fundamental basis for interpreting the engineering behaviour of the bentonite under different chemical environments. Since the mineralogical composition, specific surface area, and surface charge characteristics directly control water adsorption, swelling, compressibility, and permeability, the subsequent sections evaluate how these intrinsic features translate into macro-scale geotechnical responses. The following subsections present a detailed assessment of water content evolution, Atterberg limits, compaction characteristics, swelling behaviour, consolidation parameters, mechanical strength, and hydraulic conductivity, enabling a comprehensive understanding of bentonite performance as a landfill liner material under varying chemical conditions.

4.2 Water content and flow behavior

The results in table 3 clearly demonstrate the strong control of chemical environment on bentonite hydration. In NaCl solutions, water content decreases progressively from 52.94% at 0.1 M to 50% at 1.0 M, reflecting compression of the diffuse double layer with increasing monovalent electrolyte concentration (Mitchell & Soga, 2005). Similar suppression of hydration at high NaCl levels has been reported by Yong et al. (2012), who attributed the reduction in swelling to platelet aggregation. The drop in blow count to 31 at 1.0 M confirms reduced plasticity and a shift toward a more rigid, aggregated fabric.

Table 2. Water content and number of blows for treated bentonite

Chemical	Water Content (%)	No. of Blows (N)
0.1 M NaCl	52.94	43
0.5 M NaCl	51.72	45
1.0 M NaCl	50.00	31
0.1 M CaCl ₂	66.67	39
0.5 M CaCl ₂	57.14	33
1.0 M CaCl ₂	47.06	34
Synthetic leachate	50.00	44

CaCl₂ treatments show a contrasting, non-monotonic trend characteristic of divalent-clay interactions. At 0.1 M, the water content peaks at 66.67%, consistent with partial Na⁺-Ca²⁺ exchange that induces edge face associations and enhanced bound-water layers (Sridharan & Prakash, 1998). However, at higher concentrations (0.5-1.0 M), water content decreases sharply (57.14% to 47.06%), indicating interlayer collapse due to strong Ca²⁺ bridging and suppression of osmotic swelling (Komine & Ogata, 2004). Corresponding reductions in blow count reinforce the development of a dense, low-hydration microstructure.

The synthetic leachate sample shows an intermediate response (50% water content; 44 blows), which reflects the combined influence of mixed monovalent/divalent ions and organic ligands. Such mixtures are known to moderate clay collapse by competing for exchange sites and stabilizing hydration shells (Chen et al., 2019). Hence, the leachate-treated bentonite exhibits plasticity comparable to moderate NaCl treatments but avoids the structural rigidity observed in high-Ca²⁺ solutions. Overall, the flow behavior mirrors the hydration trends: NaCl progressively reduces plasticity, CaCl₂ induces strong flocculation at higher molarity, and leachate produces a buffered intermediate state. These patterns align well with previous reports on electrolyte-induced modifications to the consistency behavior of montmorillonite (Sharma & Sivapullaiiah, 2016), validating the mechanisms observed in this study.

4.3 Atterberg limits and consistency indices

The Atterberg limit results (Table 4) indicate that chemical environment strongly governs the plasticity behavior of bentonite. The liquid limit (LL) remains relatively unchanged across treatments (53-55%), suggesting that the high-moisture water-holding capacity of the clay is largely preserved even under elevated ionic strength. In contrast, the plastic limit (PL) shows substantial variation, reflecting sensitivity to microstructural rearrangements and changes in interparticle forces.

Table 3. Atterberg limits under chemical treatment

Chemical	LL (%)	PL (%)	PI (%)	CI	LI
0.1 M NaCl	53.0	33.3	19.7	1.0	0.0
0.5 M NaCl	54.0	25.0	29.0	0.62	1.03
1.0 M NaCl	55.0	60.0	-5.0	-0.24	N/A
0.1 M CaCl ₂	54.0	15.0	39.0	0.51	1.00
0.5 M CaCl ₂	54.0	22.2	31.8	0.68	0.43
1.0 M CaCl ₂	54.0	28.6	25.4	0.72	0.28
Synthetic leachate	54.0	35.8	18.2	1.00	0.00

In NaCl solutions, increasing concentration progressively raises the PL from 33.3% at 0.1 M to 60% at 1.0 M resulting in a negative plasticity index (PI = -5%). This phenomenon, where PL exceeds LL, is a well-documented indicator of suppressed plasticity caused by platelet aggregation and collapse of diffuse double layers (Yong & Warkentin, 1975). Di Maio (1996) reported similar behavior for Na-montmorillonite under high monovalent electrolyte concentrations, where flocculated structures lose conventional plastic response. The consistency index (CI = -0.24) for 1.0 M NaCl further confirms a transition to a brittle, non-plastic state. CaCl₂ exhibits a different trend consistent with divalent cation effects. The high PI at 0.1 M (39.0%) indicates enhanced interparticle attraction due to Ca²⁺ exchange, producing a more coherent fabric. However, increasing CaCl₂ concentration reduces PI to 25.4% at 1.0 M, reflecting progressive interlayer collapse and formation of a denser flocculated structure, in agreement with classical findings on Ca-montmorillonite behavior (Di Maio, 1996; Sridharan & Prakash, 1998). Corresponding reductions in liquidity index (LI) signify diminishing plastic workability. The synthetic leachate produces an intermediate response (PI = 18.2%), consistent with competing effects of monovalent/divalent ions, organics, and trace metals that partially buffer fabric collapse. This behavior aligns with observations by Chen et al. (2019), who noted moderated loss of plasticity in bentonite exposed to real landfill leachates.

4.4 Compaction behavior

Table 4. Standard Proctor dry densities.

Chemical	Wet Soil Weight (g)	Dry Soil Weight (g)	Dry Density (kN m ⁻³)
0.1 M NaCl	56.5	52.0	13.44
0.5 M NaCl	64.0	56.5	13.83
1.0 M NaCl	57.0	52.0	14.52
0.1 M CaCl ₂	32.0	30.0	12.65
0.5 M CaCl ₂	31.0	27.0	12.75
1.0 M CaCl ₂	44.0	40.0	13.14
Synthetic leachate	52.0	47.5	13.24

The compaction data presented in Table 4 show a clear influence of chemical composition on the densification of bentonite. In the samples treated with NaCl, dry density increases consistently with ionic strength, rising from 13.44 to 14.52 kN/m³. This trend suggests that sodium ions suppress the diffuse double layer and promote closer particle packing during compaction. Such behavior aligns with the classical understanding of double-layer compression described by Sridharan et al. (2000), where monovalent ions facilitate a dispersed fabric that collapses efficiently under mechanical energy.

The CaCl₂-treated samples exhibit a different pattern, with relatively lower dry densities at 0.1 M and 0.5 M (12.65–12.75 kN/m³). This response is characteristic of the strong flocculation induced by divalent calcium ions, which create a card-house type structure that resists compression and limits densification. A slight increase at 1.0 M CaCl₂ suggests partial breakdown of the flocculated structure under higher chemical loading, consistent with the observations made by Di Maio (1996) on calcium-dominated bentonites.

The synthetic leachate produces an intermediate dry density of 13.24 kN/m³, reflecting the combined action of various ions present in the fluid. Mixed electrolytes often lead to complex microstructural arrangements where both dispersive and flocculating forces operate simultaneously. Similar intermediate compaction states have been reported by Kolay and Singh (2019), who noted that chemically mixed environments create non-linear packing behavior in bentonite.

4.5 Swell index

The swell index values in Table 5 illustrate how bentonite’s volumetric response shifts under different chemical environments. The NaCl treated samples show a gradual decline in swelling from 41.67 % at 0.1 M to 25 percent at 1.0 M, indicating that increasing concentrations of monovalent ions suppress interlayer expansion by compressing the diffuse double layer. This type of controlled reduction is commonly reported for sodium-rich bentonites exposed to saline solutions, where changes occur but the fundamental expandability is retained (Mitchell and Soga, 2005).

The CaCl₂ results reveal a much sharper decline, from 25 percent swelling at 0.1 M down to a negative value at 1.0 M, indicating true volume contraction. This behavior reflects the strong affinity of calcium ions for exchange sites, which promotes interlayer collapse and fabric aggregation. The negative swell index suggests irreversible structural changes consistent with the findings of Di Maio (1996) and Jo et al. (2005), who observed that calcium-dominated chemical environments can eliminate the self-sealing characteristics typically associated with bentonite.

Table 5. Swell index.

Chemical	Initial Volume (ml)	Final Volume (ml)	Swell Index (%)
0.1 M NaCl	12	17	41.67
0.5 M NaCl	12	16	33.33
1.0 M NaCl	12	15	25.00
0.1 M CaCl ₂	12	15	25.00
0.5 M CaCl ₂	12	13.5	12.50
1.0 M CaCl ₂	12	11	-8.33
Synthetic leachate	12	16	33.33

In contrast, the synthetic leachate allows swelling to rebound to 33.33 percent. This intermediate behavior indicates that the mixture of ions and organic components present in leachate does not fully replicate the flocculating influence of pure calcium solutions. Instead, the competing chemical species limit complete particle aggregation, allowing the bentonite to maintain a significant proportion of its swelling potential. This outcome highlights the complex and often non-linear response of bentonite in real-world waste containment environments where multiple contaminants coexist.

4.6 Compressibility and consolidation

The consolidation response of the bentonite under a vertical stress of 25 kPa shows clear evidence of chemically driven modifications in particle arrangement and compressibility. The volume change values in Table 6 reveal a gradual increase in compressibility with rising salt concentration for both NaCl and CaCl₂ solutions. For NaCl, the volume reduction progresses from 9.17 percent at 0.1 M to 12.5 percent at 1.0 M, which is consistent with the expected collapse of diffuse double layers as electrolyte concentration increases. This thinning of repulsive forces allows particles to approach more closely during consolidation, a trend that aligns with classical electrochemical principles described by Mesri and Olson (1971).

Table 6. Compression data under 25 kPa stress.

Chemical	Initial Vol (ml)	Final Vol (ml)	Volume Change (%)	Compression Index(Cc)
Synthetic Leachate	12.0	11.0	-8.33	0.40
0.1 M NaCl	12.0	10.9	-9.17	0.45
0.5 M NaCl	12.0	10.7	-10.00	0.50
1.0 M NaCl	12.0	10.5	-12.50	0.55
0.1 M CaCl ₂	12.0	10.8	-10.00	0.50
0.5 M CaCl ₂	12.0	10.5	-12.50	0.55
1.0 M CaCl ₂	12.0	10.0	-16.67	0.60

Calcium chloride exhibits a more pronounced effect: the sample compressed by more than 16 percent at 1.0 M, reflecting the strong capacity of Ca²⁺ ions to promote interparticle bonding and structural aggregation. Such flocculated fabrics can initially appear rigid but undergo significant collapse under load once the particle network begins to rearrange. This type of chemically induced metastability has been widely reported in studies of divalent ion-treated bentonites and is associated with long-term settlement under sustained stresses. The void ratio data in Table 7 support this interpretation. While all samples were subjected to the same applied stress, the resulting void ratios differ substantially, with NaCl-treated soils reaching e values as low as 1.10 and CaCl₂-treated soils descending to e = 1.00 at the highest concentration. These reductions indicate not merely densification but a transformation in the packing mode of clay aggregates. The NaCl systems tend toward compact, dispersed structures, whereas CaCl₂ encourages particle-edge associations that collapse under load, altering permeability pathways and compressibility behavior.

Table 7. Void ratio and log stress

Chemical	Stress (kPa)	Void Ratio (e)	Log (Stress)
Synthetic leachate	25	1.50	1.398
0.1 M NaCl	25	1.35	1.398
0.5 M NaCl	25	1.30	1.398
1.0 M NaCl	25	1.10	1.398
0.1 M CaCl ₂	25	1.20	1.398
0.5 M CaCl ₂	25	1.15	1.398
1.0 M CaCl ₂	25	1.00	1.398

The parameters in Table 9 further reinforce these trends. The compression index (Cc) increases steadily with salt concentration for both electrolytes, reaching 0.75 for 1.0 M NaCl and 0.80 for 1.0 M CaCl₂. The higher Cc values for divalent ions at comparable molarities reflect their stronger influence on interlayer water removal and particle clustering. Corresponding decreases in the recompression index (Cr) indicate diminishing elastic recovery capacity, suggesting that chemically conditioned bentonite becomes progressively more prone to permanent deformation. Additionally, the pre-consolidation pressures (σ'c) consistently drop as concentration increases, particularly for CaCl₂, implying that the soil loses its inherent resistance to structural collapse and becomes susceptible to yielding under lower stresses.

Table 9. Cc, Cr, and σ'c (author data).

Chemical	Initial e	Final e	Cc	Cr	σ'c (kPa)
Synthetic leachate	1.50	1.20	0.45	0.40	80
0.1 M NaCl	1.35	1.15	0.55	0.30	70
0.5 M NaCl	1.30	1.05	0.60	0.25	65
1.0 M NaCl	1.10	1.00	0.75	0.20	60
0.1 M CaCl ₂	1.20	1.05	0.50	0.30	72
0.5 M CaCl ₂	1.15	1.00	0.65	0.25	68
1.0 M CaCl ₂	1.00	0.95	0.80	0.15	55

Together, these results illustrate a systematic weakening of the soil's consolidation resistance under stronger ionic environments. The observed behavior is in good agreement with the frameworks proposed by Nagaraj and Srinivasa Murthy (1986), who emphasize the role of ion-induced microstructural evolution in governing compressibility and long-term settlement.

4.7 Mechanical performance and failure modes

The mechanical test outcomes show that bentonite responds very differently depending on the type and concentration of the chemical environment. Samples exposed to synthetic leachate and low concentrations of NaCl develop relatively higher peak loads and maintain gradual, progressive failure. These specimens undergo deformation over longer strain intervals, and the multiple divisions recorded during the test indicate a more ductile mode where the soil continues to redistribute load even after peak resistance. As salt concentration increases, however, the ability of the material to carry load declines noticeably. For NaCl, this decline is steady, with peak stress falling from 0.229 kg/cm² at 0.1 M to 0.089 kg/cm² at 1.0 M.

Table 10. UCS / mechanical test summary

Parameter	Synthetic Leachate	NaCl 0.1M	NaCl 0.5M	NaCl 1.0M	CaCl ₂ 0.1M	CaCl ₂ 0.5M	CaCl ₂ 1.0M
Total divisions	8	16	15	15.5	18	18	10
Peak load (kg)	2.4	2.6	1.8	1.02	1.7	0.85	0.35
Max compressive stress (kg/cm ²)	0.211	0.229	0.158	0.089	0.149	0.074	0.031
Deformation at peak (mm)	80	97	92	97	97	92	77
Strain at peak	0.0088	0.0108	0.0103	0.0088	0.0108	0.0103	0.0088
Final stress value	0.102	0.089	0.048	0.021	0.071	0.031	0.008

Calcium chloride has a much stronger impact. The 1.0 M CaCl₂ sample reaches only 0.031 kg/cm² at peak stress and shows one of the lowest residual strengths in the test series. Instead of spreading deformation across the specimen, high-Ca²⁺ samples tend to fail suddenly and cleanly, producing only a few divisions and leaving the material with almost no post-peak resistance. The transition from gradual to abrupt failure as Ca²⁺ concentration increases mirrors earlier observations reported in contamination-induced strength reduction studies. Overall, these results indicate that the structural integrity of bentonite is most compromised in divalent environments, especially when salt levels are high.

4.8 Settlement and hydraulic behavior

Settlement responses also reflect the contrasting influence of monovalent and divalent salts. All chemically treated samples show substantial settlement under loading, but the magnitude and rate differ. The highest values appear for NaCl at 1.0 M, where settlement approaches 85 percent, suggesting that the fabric becomes more easily compressible once the soil structure has adjusted to the electrolyte. Calcium chloride again demonstrates its stronger effect: although the settlement percentage at 1.0 M is slightly lower than for NaCl, the consolidation proceeds very quickly, indicating that the soil structure accommodates deformation with little resistance.

Table 11. Settlement behavior

Sample	% Settlement	Cv	K (interpretation)
CaCl ₂ 1.0 M	~81%	High	Moderate-High
CaCl ₂ 0.5 M	~80%	High	Moderate
CaCl ₂ 0.1 M	~79%	Moderate	Lower
NaCl 1.0 M	~85%	High	Moderate
NaCl 0.5 M	~78%	Moderate	Lower
NaCl 0.1 M	~80%	Lower	Lowest
Synthetic leachate	~76%	Moderate	Lower

Differences in Cv and the interpreted hydraulic conductivity values emphasize these tendencies. High Cv is consistently associated with CaCl₂-treated samples, reflecting rapid dissipation of pore water pressures and suggesting the development of more open drainage pathways as chemical concentration increases. The synthetic leachate behaves more moderately, with settlement near 76 percent and slower consolidation characteristics. This behavior likely arises because the mixture of ions does not allow the soil to reorganize as uniformly as in the single-electrolyte cases. When combined with earlier observations on compressibility and pre-consolidation pressures, the settlement data reinforce the expectation that long-term sealing performance deteriorates more rapidly in salt-rich environments, particularly where Ca²⁺ dominates. The results collectively show that bentonite behavior under chemical exposure is controlled by coupled changes in hydration, fabric arrangement, and interparticle bonding rather than by any single geotechnical parameter. Variations in water content, plasticity, swelling, compressibility, strength, and settlement consistently reflect the nature and concentration of the interacting ions. Monovalent sodium solutions primarily modify bentonite through diffuse double layer compression and densification, whereas divalent calcium solutions induce pronounced fabric reorganization, interlayer collapse, and loss of mechanical resilience. The synthetic leachate produces an intermediate response, highlighting the role of mixed ionic chemistry in moderating extreme structural changes. These interrelated trends indicate that chemical exposure governs both short-term mechanical response and long-term hydraulic stability, providing a coherent basis for synthesizing the overall implications for landfill liner performance in the concluding section.

4. Conclusions

The results confirm that chemical attack significantly alters the long-term deformation and strength characteristics of bentonite liners. While monovalent salts primarily induce reversible densification through diffuse double layer compression, divalent cations trigger irreversible fabric collapse, swelling loss, and strength degradation. The observed reductions in swelling capacity (>80%), pre-consolidation pressure (up to 30%), and compressive strength (>60%) under Ca²⁺ exposure directly translate to increased settlement potential and loss of barrier reliability. The novelty of this study lies in quantifying these degradation pathways across coupled hydraulic, mechanical, and consolidation responses, providing engineering-relevant thresholds for assessing liner durability in chemically aggressive geological environments.

Declaration of competing interest: The authors declare no competing financial interests.

References

- Al-Qatif, A., Hassan, M., Al-Amoudi, O., Khan, A., & Al-Dosari, A. (2021). Effect of fluid chemistry on the consolidation and hydraulic conductivity of sand-clay liners. *Sustainability*, 13, 11213.
- Bohnhoff, G., Shackelford, C. D., & Pusch, R. (2003). Chemical modification of bentonite for engineered barriers: multiswellable bentonite and polymer nanocomposites. *GeoCongress Proceedings*.

3. Chen, W. Q., Sedighi, M., & Jivkov, A. P. (2023). Elevated temperature effects on interfacial water and swelling of Na-montmorillonite. arXiv.
4. Chittoori, B. C. S., Sivapullaiah, P. V., & Reddy, B. V. V. (2018). Clay mineralogical effects on the hydraulic behaviour of engineered liners. *Applied Clay Science*.
5. Cui, Y.-J., Tang, A.-M., Loiseau, C., & Delage, P. (2008). Unsaturated hydraulic conductivity of a sand-bentonite mixture under constant volume and free-swell conditions. *Engineering Geology*.
6. Daniel, D. E. (1984). Geotechnical aspects of clay liners. *Journal of Geotechnical Engineering*.
7. De Camillis, S., Di Emidio, G., Bezuijen, A., & Flores, C. (2018). Chemical interactions in GCLs under leachate. *Geosynthetics International*.
8. Di Maio, C. (1996). Chemical deterioration of bentonite in salt solutions. *Engineering Geology*.
9. Egloffstein, T. (2001). Natural clay barriers in chemical environments. *Applied Clay Science*.
10. Fan, R.-D., Reddy, K. R., Yang, Y.-L., & Du, Y.-J. (2020). Index properties, hydraulic conductivity and contaminant-compatibility of CMC-treated sodium activated calcium bentonite. *Int. J. Environ. Res. Public Health*, 17, 1863.
11. Gates, W. (2003). Divalent cation effects on bentonite fabric and permeability. *Soils and Foundations*.
12. Hu, Y.-Y., & Yuan, S.-H. (2023). Constitutive theory of saturated porous media considering porosity-dependent skeleton strain and chemical activity. *Computational Mechanics*.
13. Jo, H. Y., Katsumi, T., Benson, C. H., & Edil, T. B. (2001). Hydraulic properties of clays exposed to chemicals. *Geosynthetics International*.
14. Jo, H. Y., Benson, C. H., Edil, T. B., & Montoya, B. (2005). Chemical compatibility of soil-bentonite mixtures. *J. Geotechnical & Geoenvironmental Eng.*
15. Kan, A. T., & Tomson, M. B. (2001). Heavy metal precipitation on clay minerals. *Environ. Sci. Technol.*
16. Karland, O., Olsson, S., & Nilsson, U. (2006). Long-term performance of bentonite in engineered barriers under Ca²⁺ exposure. *Applied Clay Science*.
17. Katsumi, T., Benson, C. H., & Edil, T. B. (2007). Effect of salt solutions on geosynthetic clay liners. *Geosynthetics Int.*, 14(6), 318–329.
18. Kaya, S., & Fang, H. (2000). Plasticity index variations in saline clays. *Clays and Clay Minerals*.
19. Kenney, T. C., et al. (1992). Brittleness and failure modes of swelling clays. *J. Geotechnical Eng.*
20. Kaoser, H., Chen, X., Khan, A., & Li, L. (2022). Swelling performance of raw and modified bentonite exposed to synthetic E-waste leachate. *Sci. Reports*.
21. Loiseau, C., Cui, Y.-J., & Tang, A.-M. (2010). Volume change behaviour of highly compacted bentonite. *Engineering Geology*.
22. Mesri, G., & Olson, R. E. (1971). Influence of electrolyte concentration on consolidation of clays. *Journal of Soil Mechanics & Foundations Div.*
23. Mitchell, J. K., & Soga, K. (2005). *Fundamentals of Soil Behavior*. John Wiley & Sons.
24. Mitra, A., et al. (2016). Long-term durability of bentonite barriers under multivalent ions. *Clay Minerals Journal*.
25. Nagaraj, H. B., & Srinivasa Murthy, V. (1986). Consolidation properties of chemically treated clays. *Soils and Foundations*.
26. Naik, R., Dodagoudar, G. R., & Reddy, K. R. (2021). Evaluation of Indian bentonite for landfill liner application. *J. Hazardous Materials*.
27. Ningming, C., et al. (2022). Mg/Ca effects on bentonite swelling. *Applied Clay Science*.
28. Onikata, M., Hayashi, S., & Taki, K. (1999). Multiswellable bentonite for chemically aggressive environments. *Applied Geochemistry*.
29. Pusch, R. (1982). Microstructure of bentonite in engineered barriers. *Geotechnique*.
30. Puppala, A. J., et al. (2016). Chemical stabilization effects on Cv. *J. Geotechnical Eng.*
31. Prongmanee, N., et al. (2018). Polymerized bentonite permeability in NaCl and CaCl₂.
32. *Lowland Technology Int.*
33. Rao, A. S., & Shivananda, R. (2005). Sodium and calcium exchange effects on clay compaction and permeability. *Indian Geotechnical Journal*.
34. Razakamanantsoa, A., & Di Emidio, G. (2012). Na-bentonite stabilization by chloride salts. *Applied Clay Science*.
35. *RSC Advances* (2020). Attenuation of heavy metals in leachates by bentonite-polymer composites.
36. Rowe, R. K. (2014). Long-term performance of clay liners. *Canadian Geotechnical Journal*.
37. Salemi, A., et al. (2020). Ion-specific effects on bentonite permeability. *Clays & Clay Minerals*.
38. Scalia, A., et al. (2018). Nanodispersible modified bentonite. *Nanomaterials*.
39. Shackelford, C. D. (1994). Waste-soil interactions that alter hydraulic conductivity. *Waste Containment Systems*.
40. Shackelford, C. D., & Daniel, D. E. (2000). Clay-chemical interactions and liner performance influence. *J. Geotechnical & Geoenvironmental Eng.*
41. Sposito, G. (1984). *The Surface Chemistry of Soils*. Oxford University Press.
42. Sridharan, A., & Nagaraj, H. B. (2000). Role of exchangeable cations in clay behaviour.
43. *Clays and Clay Minerals*.
44. Sato, Y., et al. (2017). Aging effects on GCL performance. *Geotextiles & Geomembranes*.
45. Tan, S. A., et al. (2017). Cation exchange influence on hydraulic conductivity of bentonite.
46. *Applied Geochemistry*.
47. van Olphen, H. (1977). *An Introduction to Clay Colloid Chemistry*. Wiley.
48. Wigger, C., & van Loon, L. R. (2001). Influence of chemical solutions on bentonite hydraulic conductivity. *Geotechnical Barriers*.
49. Yong, R. N., & Warkentin, B. P. (1975). *Introduction to Soil Behaviour*. Pergamon Press.
50. Zhang, X., et al. (2019). Particle flocculation and mechanical behavior in salt-affected bentonite. *Geomechanics Journal*.
51. Di Emidio, G., et al. (2015). HYPER clay and chemical compatibility. *GeoCongress Proceedings*.
52. Bohnhoff, G., Onikata, & Hayashi (1996). Propylene carbonate activation of bentonite.
53. *Geosynthetics International*.
54. Chen, W., Jivkov, A., & Sedighi, M. (2022). High-temperature swelling behaviour of montmorillonite. *J. Phys. Chem. C*.
55. Mitina, N. V., & Vlasov, L. (2013). Heavy metal immobilization by clays. *Environmental Engineering Journal*.
56. Kan, A. T., Tomson, M. B., & O'Connor, C. T. (1999). Adsorption and precipitation mechanisms on clay surfaces. *Environ. Sci. Technol.*
57. Katsumi, T., et al. (2008). Ionic strength and bentonite permeability. *Geotechnique*.
58. Taylor, M., & Carson, M. (2017). Geotechnical performance of modified bentonite liners.
59. *Journal of Geotextiles*.
60. Bhattacharyya, A., et al. (2016). Bentonite mineralogy and swelling in Indian deposits.
61. *Applied Clay Science*.
62. Kumar, S., & Singh, R. (2019). Acid attack on clay liners: mechanisms and mitigation.
63. *Environmental Geotechnics*.
64. Park, S. H., et al. (2015). Polymer treatment of bentonite for improved chemical compatibility. *Journal of Hazardous Materials*.
65. Zheng, Y., et al. (2020). Long-term evolution of bentonite under leachate exposure.
66. *Environmental Science & Technology*.
67. Lopes, C., & Pereira, J. (2018). Microstructure of flocculated vs dispersed bentonites. *Applied Clay Science*.
68. Ulrich, C., & Brown, L. (2014). Comparative study of salt vs acid ageing of bentonite. *Geotechnical Testing Journal*.
69. Gomez, R., et al. (2013). Effect of heavy metals on consolidation behaviour. *Soils and Foundations*.
70. Swart, P., et al. (2021). Sealing performance of polymer modified bentonites. *Clays & Clay Minerals*.
71. Reddy, M. S., & Ashwin, S. (2018). Chemical compatibility testing protocols for landfill liners. *Waste Management*.
72. Li, Q., et al. (2017). Permeability increases in Ca-treated bentonite: an experimental study.
73. *Applied Clay Science*.
74. Sarker, P., & Das, B. (2019). Role of pH in bentonite deterioration. *Journal of Environmental Geotechnics*.
75. Chen, Y., Liu, X., & Liu, J. (2019). Influence of landfill leachate on the swelling behavior and microstructure of bentonite. *Applied Clay Science*, 168, 1–10.
76. Komine, H., & Ogata, N. (2004). Experimental study on swelling characteristics of compacted bentonite. *Canadian Geotechnical Journal*, 41(2), 326–337.
77. Mitchell, J. K., & Soga, K. (2005). *Fundamentals of Soil Behavior*. John Wiley & Sons.
78. Sharma, R. S., & Sivapullaiah, P. V. (2016). Influence of electrolytes on the consistency limits of bentonites. *Geotechnical and Geological Engineering*, 34(5), 1551–1562.
79. Sridharan, A., & Prakash, K. (1998). Mechanism controlling the liquid limit of clays. *Clays and Clay Minerals*, 46(4), 465–471.
80. Yong, R. N., Mohamed, A. M. O., & Warkentin, B. P. (2012). *Principles of Contaminant Transport in Soils*. Elsevier.
81. Chen, Y., Liu, X., & Liu, J. (2019). *Applied Clay Science*, 168, 1–10.
82. Di Maio, C. (1996). Exposure of bentonite to salt solutions. *Engineering Geology*, 43(2), 1–17.
83. Sridharan, A., & Prakash, K. (1998). *Clays and Clay Minerals*, 46(4), 465–471.
84. Yong, R. N., & Warkentin, B. P. (1975). *Soil Properties and Behaviour*.
85. Chen, Y., Liu, X., & Liu, J. (2019). *Applied Clay Science*, 168, 1–10.
86. Di Maio, C. (1996). *Engineering Geology*, 43, 1–17.
87. Rao, S. M., & Thyagaraj, T. (2007). *Clays and Clay Minerals*, 55(5), 403–410.
88. Sridharan, A., Nagaraj, H. B., & Sivapullaiah, P. V. (2000). *Canadian Geotechnical Journal*, 37(5), 1220–1230.
89. Sridharan, A., & Prakash, K. (2000). *Geotechnical Testing Journal*, 23(1), 35–43.