

Structure, Properties and Hydration of Homoionic Saturated Montmorillonite

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Kurzfassung

Diese Studie untersucht das strukturelle, energetische und hydrationsabhängige Verhalten von Na^+ , K^+ , Ca^{2+} und Mg^{2+} -gesättigten Montmorilloniten durch die Kombination von Dichtefunktionaltheorie-Simulationen (DFT-D3) mit experimentellen Charakterisierungen natürlicher Tone (CalciGel und Secursol UHP). Die rechnerischen Analysen zeigen, dass die Zwischenschichtkationen einen entscheidenden Einfluss auf Stabilität, Quellverhalten und mechanische Eigenschaften ausüben. Na^+ - und Ca^{2+} -homoionisch gesättigte Montmorillonite erweisen sich als die stabilsten, während K^+ - und Mg^{2+} -homoionisch gesättigte Montmorillonite eine geringere Stabilität aufweisen. Die Minimierung der Gesamtenergie zeigt, dass elektrostatische und Dispersionswechselwirkungen, und nicht allein der Ionenradius, das strukturelle Gleichgewicht bestimmen. Der Basalabstand (d_{001}) nimmt mit zunehmender Kationengröße zu ($\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$), während die Dicke der 2:1-Schicht nahezu konstant bleibt. Das berechnete Kompressionsmodul liegt zwischen 20 und 75 GPa, wobei Na^+ -homoionisch gesättigte Montmorillonite die höchste Steifigkeit und K^+ -homoionisch gesättigte Montmorillonite die niedrigste aufweist. Die Energielandschaftsanalysen (E-Map) zeigen ferner, dass einwertige Kationen gleichmäßigere Potentialverteilungen und eine höhere Mobilität besitzen, während zweiwertige Kationen aufgrund stärkerer elektrostatischer Anziehung bevorzugt in der Nähe negativ geladener Bereiche lokalisiert sind. Hydratation verringert die Energiebarrieren für die Ionenmigration deutlich, da Wassermoleküle Hydrathüllen bilden, die die Diffusion in der Zwischenschicht erleichtern. Der Mobilitätstrend folgt der Reihenfolge $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ und verdeutlicht die zentrale Rolle der Hydratation beim Ionenaustausch und Quellverhalten.

DFT-Simulationen des Quellverhaltens offenbaren schrittweise Hydratationsübergänge von Monolagen (1W) zu Doppellagen-Konfigurationen (2W). Einwertige Kationen ermöglichen aufgrund geringerer Oberflächenanziehung größere Zwischenschichtausdehnungen, während zweiwertige Kationen das Quellen durch stärkere elektrostatische Bindung begrenzen. Mit zunehmendem Wassergehalt verschiebt sich die dominante Wechselwirkung von der Kation–Oberflächen-Anziehung hin zur Wasserstoffbrückenbindung zwischen Wassermolekülen, was zu diskreten Zunahmen des Basalabstands führt. Experimentelle Untersuchungen an CalciGel und Secursol UHP bestätigen diese rechnerischen Ergebnisse. Secursol UHP weist einen höheren smektitischen Anteil, eine größere Kationenaustauschkapazität und eine stärkere Wasseraufnahme im Vergleich zu CalciGel auf. Na^+ - und Mg^{2+} -homoionisch gesättigte Montmorillonite zeigen das höchste Quellvermögen, während K^+ -homoionisch gesättigte Montmorillonite aufgrund geringer Hydratationsenergie eine eingeschränkte Expansion aufweist. Die XRD-Analyse zeigt hysteretische Hydratations- und Dehydratationsprozesse, Wasserrückhaltung in Mesoporen sowie eine stufenweise Zwischenschichtquellung von 0W- zu 3W-ähnlichen Zuständen mit zunehmender relativer Luftfeuchtigkeit.

Insgesamt etabliert diese Arbeit den grundlegenden Zusammenhang zwischen Kationenvaleanz, Hydratationsenergie und Zwischenschicht-Elektrostatik als bestimmende Faktoren für die strukturellen, mechanischen und transportbezogenen Eigenschaften homoionisch gesättigter Montmorillonite. Der integrierte rechnerische und experimentelle Ansatz liefert eine belastbare Grundlage für die Entwicklung fortschrittlicher tonbasierter Materialien für Umwelt-, geotechnische und Ionenaustauschanwendungen.

Abstract

This study explores the structural, energetic, and hydration dependent behavior of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} -saturated montmorillonites by combining Density Functional Theory (DFT-D3) simulations with experimental characterization of natural clays (Calcigel and Secursol UHP). Computational analyses show that the interlayer cations exert a decisive influence on the stability, swelling, and mechanical response. Na^+ and Ca^{2+} -homoionic saturated montmorillonite are the most stable, while K^+ and Mg^{2+} exhibit lower stability. Total energy minimization reveals that electrostatic and dispersion interactions, rather than ionic radius alone, govern structural equilibrium. Basal spacing (d_{001}) increases with cation size ($\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$), and the 2:1 layer thickness remains nearly constant. The computed bulk modulus varies between 20 and 75 GPa, with Na^+ -homoionic saturated montmorillonite showing the highest stiffness and K^+ -homoionic saturated montmorillonite the lowest. Energy mapping (E-Map) further indicates that monovalent cations possess more uniform potential distributions and greater mobility, whereas divalent cations localize near negatively charged regions due to their stronger electrostatic attraction. Hydration markedly reduces energy barriers for ion migration as water molecules form hydration shells, facilitating diffusion within the interlayer. The mobility trend follows $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$, highlighting the key role of hydration in ion exchange and swelling.

DFT simulations of swelling reveal stepwise hydration transitions from monolayer (1W) to bilayer (2W) configurations. Monovalent cations enable larger interlayer expansion due to weaker surface attraction, while divalent cations restrict swelling through stronger electrostatic binding. Increasing water content shifts the dominant interactions from cation–surface attraction to hydrogen bonding between water molecules, resulting in discrete increases in basal spacing. Experimental studies on Calcigel and Secursol UHP confirm these computational results. Secursol UHP shows a finer smectitic fraction, higher cation-exchange capacity, and greater water retention than Calcigel. Na^+ - and Mg^{2+} -homoionic saturated montmorillonite exhibit the highest swelling, whereas K^+ -homoionic saturated montmorillonite limits expansion due to low hydration energy. XRD reveals hysteretic hydration–dehydration, water retention in mesopores, and stepwise interlayer swelling from 0W- to 3W-like states as relative humidity increases.

Overall, this work establishes the fundamental relationship between cation valence, hydration energy, and interlayer electrostatics in determining structural, mechanical, and transport properties of homoionic saturated montmorillonite. The integrated computational and experimental approach provides a strong foundation for designing advanced clay-based materials for environmental, geotechnical, and ion-exchange applications.

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1 Introduction

1.1 Introduction

Clays are naturally occurring materials primarily composed of fine-grained minerals and other associated phases. Bentonites are types of clay formed from the alteration of volcanic rock, and their main components are smectite group minerals, most often montmorillonite (Guggenheim and Martin, 1995; Bergaya and Lagaly, 2006). Montmorillonite is a phyllosilicate clay mineral with a unique 2:1 layer structure (two tetrahedral sheets sandwiching one octahedral sheet), high surface area, porosity, and cation exchange capacity (CEC) due to isomorphous substitution. These properties allow it to adsorb water, swell, and retain cations, making bentonite useful as filler, binder or absorbent in various applications, such as: foods and beverages, fertilizer, water purification, water remediation, catalysts, drilling mud, bleaching earth and buffer materials. Currently and also in the future, bentonite is the main candidate materials for use as a nuclear waste disposal which serves as a densely packed absorbent/adsorbent to retard the migration of pore water and radionuclides (Pusch, 1992). Compacted bentonite serves as a crucial multi-barrier component in high-level nuclear waste repositories, where its montmorillonite content swells upon contact with water to create a highly impermeable, self-sealing barrier. This swelling minimizes water flow and prevents the escape of radionuclides by blocking their migration through the engineered barrier system and the surrounding geology. Additionally, the bentonite's chemical properties allow it to absorb and immobilize radionuclides, further confining them within the repository. In addition, montmorillonite is also studied as montmorillonite-based two-dimensional (2D) functional materials that play an important role in pollution adsorption, medical antibacterial uses, thermal conduction, flame-retardant, slow-release drugs and fertilizers. The preparation of montmorillonite-based two-dimensional nanocomposites also has promising future prospects in photocatalysis and wastewater treatment (Gaharwar et al., 2019; Wang et al., 2021; Turunen et al., 2022).

Montmorillonite swells by adsorbing water between its layers, a process influenced by type of interlayer cation, crystal structure, and surface interactions. The type of interlayer cation influences through its hydration energy, ionic size, and type of coordination. The charge density and location of charges within the crystal structure impact to hydration and swelling properties. Adsorption of water onto the negatively charged of surfaces is driven by the strong electrostatic attraction between water molecules and exchangeable cations in the interlayer space.

This study examines and investigates the relationship between the structure and properties of montmorillonite and its interaction with water molecules. This study is a combination of computational modelling and experimental laboratory work. Chapter 2 discusses model structure and computational chemistry methods; methods for preparing homoionic saturated montmorillonite samples and experimental analysis methods in detail. Chapter 3 focuses on the study of optimization of homoionic saturated montmorillonite structures with different interlayer cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}), differences in layer charge ($\xi = 0.125, 0.250, 0.375$ and 0.500), octahedral structure models ($tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$) and the orientation direction of cell unit arrangements. A study was conducted

on the physical properties of the optimized homoionic saturated montmorillonite structures, including the d_{001} distance, structure stability, specific density, layer and interlayer thickness, cation position in the interlayer, OH vector orientation, elastic properties and bulk modulus. Chapter 4 focused on stability and energy mapping of the simplest structure ($\xi = 0.500$) with different interlayer cation types and octahedral structures. The results of energy mapping used to examine the position and mobility of interlayer cations in homoionic saturated and hydrated montmorillonite. Chapter 5 focuses on the interaction between montmorillonite and water, effect of interlayer cation type and layer charge on the hydration of homoionic montmorillonite to predict the formation of a water layer. Chapter 6 focuses on examining how water interact with two samples, Calcigel and Secursol UHP, under varying relative humidity at 20 °C, and on analysing how homoionic saturated montmorillonite (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) with different CEC capacities absorbs water.

The objective of this study is to thoroughly understand homoionic saturated montmorillonite by investigating its structure, properties, and hydration mechanisms, including ion mobility in interlayer and water adsorption, through a combination of Density Functional Theory (DFT) calculations and laboratory experiments in homoionic preparation sample and its hydration properties, with the aims to establishing a fundamental knowledge base for its technological applications.

1.2 Smectite Group

Smectite are 2:1 phyllosilicate which the structure composed in a stacked manner of tetrahedral sheets and octahedral sheets. Its crystal structure consists of one octahedral sheet between two tetrahedral sheets. The tetrahedral sheet consists of a tetrahedron basic unit structure occupied by a central atom (common tetrahedral cations are Si^{4+} and Al^{3+}) with a coordination number four times that of the oxygen atoms surrounding it. The central atom in the tetrahedron basic unit structure is surrounded by four oxygen atoms. Each tetrahedron connects with adjacent tetrahedra by sharing the three angles occupied by the basal oxygen atoms to form an infinite two-dimensional hexagonal mesh pattern in the direction of the a and b axes in the crystallographic direction (Brigatti et al, 2006). Meanwhile, the octahedral sheet consists of an octahedron basic unit structure, where the octahedron basic unit is occupied by a central metal atom (cations are generally Al^{3+} , Fe^{3+} , Mg^{2+} and Fe^{2+}) with a coordination number of six times that of the oxygen atoms surrounding it. The central atom in the octahedron basic unit structure is surrounded by six oxygen atoms. In octahedral sheets, each octahedron is connected to each other by creating shared edges. Edge-shared octahedrons form hexagonal or pseudo-hexagonal sheets of symmetry. The position of OH groups on the octahedra results in two topological differences namely *cis*- and *trans*- orientation. In *cis*-octahedron, OH groups are in the same plane while in *trans*-octahedron OH groups are on opposite sides. The OH groups are integral to its structural framework within the octahedral sheet, formed by the presence of aluminium and magnesium atoms coordinated with close-packed oxygen and hydroxyl ions.

The free corners occupied by the tetrahedral apical oxygen atoms of all tetrahedra point to the same side of the sheet and connect the tetrahedral and octahedral sheets to form a plane equal to the position of the octahedral anionic (OH). The octahedral anion is located near the centre of each tetrahedral 6-fold ring, but does not share with the tetrahedra. When tetrahedral and octahedral sheets are combined in a layer, the resulting structure can be either electrically neutral or negatively charged. Electrical neutrality exists if the octahedral sheet contains trivalent cations (R^{3+}) on two

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octahedral sites (usually Al^{3+} and Fe^{3+}), with a vacancy ($\square$) on the third octahedron $[\text{R}_2^{3+}(\text{OH})_6]$; divalent cations (R^{2+} , typically Fe^{2+} , Mg^{2+} , Mn^{2+}) occupy all octahedral sites $[\text{R}_3^{2+}(\text{OH})_6]$; and the tetrahedral sheet contains Si^{4+} in all tetrahedra.

In 2:1 layer smectites, the octahedral sheets can be dominantly occupied by trivalent cations (dioctahedral smectites) or divalent cations (trioctahedral smectites). The formula unit (FU) of smectite includes three octahedral sites. Trioctahedral smectites have three cations per unit formula, typically magnesium or iron, fully occupying the available octahedral sites. In contrast, dioctahedral smectites have only two cations per FU, often aluminium, leaving one octahedral site vacant. The oxygen atoms are shared between adjacent occupied octahedral sites and with the apical oxygens of the tetrahedral sheet (from top and bottom). The remaining oxygens in each octahedron are bonded to H^+ atoms, forming OH groups (two per FU). As a result, the dioctahedral sheet is composed of cis- and trans-octahedrons. A trans-octahedron is defined when two OH groups are located diagonally on opposite vertices, while the cis-position is defined by two hydroxyl groups on one side. Therefore, for each FU, there is one trans and two cis-positions. In dioctahedral smectite, one-third of the octahedral positions are vacant. Octahedral sheets with trans-site vacant are referred to as *trans-vacant* (*tv*) and cis-site vacant as *cis-vacant* (*cv*). In the natural state, dioctahedral smectites are generally found in *tv* and *cv* types, where montmorillonite is mainly *cv* (Tsipursky and Drits, 1984; Wolters et al., 2009).

The physical properties and chemical properties of the 2:1 layer smectite structure are influenced by the position of the cation substitution in the octahedral sheet. The position of the cation substitution in the octahedral sheet affects the interaction of the atoms in the octahedral sheet affects the interaction between the octahedral sheet and also affects the position and interaction of all atoms in the smectite structure as a whole. The position of the octahedral substitution also affects the type of vacant caused by the substitution, then the type of vacant has affects the structure and physical properties of the chemical properties of smectite. The position and number of cation substitutions in the octahedral sheet have implications for determining the number and position of cations in the interlayer and layer charge (Garcia-Romero et al., 2021).

Montmorillonite and beidellite, the most abundant smectite phases in bentonite, are distinguished from other dioctahedral smectites by the presence of isomorphic substitutions: $\text{Mg}^{2+} \rightarrow \text{Al}^{3+}$ in the octahedral sheet and $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$ in the tetrahedral sheet (Bergaya and Lagaly, 2006; Wolters et al., 2009; and Emmerich et al., 2009). The substitutions in both the tetrahedral and octahedral sheets generate a negative layer charge, which is balanced by interlayer cations. The layer charge (ξ) ranges from 0.2 to 0.6 FU, corresponding to $\text{M}_{x/v}^{\text{v}+} (\text{Si}_{4-y} \text{Al}_y) [(\text{Al}, \text{Fe}^{3+})_{2-z} (\text{Mg}, \text{Fe}^{2+})_z] \text{O}_{10} (\text{OH})_2$, where $x = \xi = y + z$, and $\text{M}^{\text{v}+}$ denotes the interlayer cations such as Na^+ , K^+ , Ca^{2+} , or Mg^{2+} (Emmerich et al., 2018). Smectites that undergo isomorphic substitution in tetrahedral sheets are called beidellite, while smectites that undergo isomorphic substitution in octahedral sheets are called montmorillonite. Isomorphic substitution causes vacancies to exist in the octahedral sheet, giving rise to a charge layer and the 2:1 layer as a whole becomes negatively charged. The charged layer is then balanced by cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) that occupy the interlayer. The layer charge difference in the 2:1 layer is determined by the number of isomorphic substitutions that occur. Interlayer cations connect adjacent layers. The cations in the interlayer can interact with polar solvents such as water. The interaction between the interlayer cations and water causes the cations to hydrate through a solvation process with ion-dipole interaction. This is called smectite hydration. The degree of hydration that occurs can

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be at different levels depending on the type of cation and the number of water molecules that can solvate the interlayer cations.

The presence of hydrated cations in the interlayer makes the cations exchangeable and the cation exchange ability of smectite is expressed in CEC. Electrostatic attraction of interlayer cations can unite the charged layers. The net layer charge per formula unit in the smectite group ranges between 0.2 and 0.6 (Newman and Brown, 1987; Guggenheim et al., 2006), some dioctahedral 2:1 layer silicates with a layer charge of 0.125 charge per formula unit that are swellable (Emmerich et al., 2018). The position of the cation substitution in the 2:1 structure affects the position of the negative charge on the layer surface (Guven, 1992). The homogeneity of interlayer cation has implications for the behaviour of hydrated cations in the interlayer space and smectite surface. Thus, for octahedral charged smectites such as montmorillonite, the negative charge is delocalized over the surface oxygen so that only weak hydrogen bonds can form with interlayer water. For tetrahedrally charged smectites such as beidellite and saponite, however, the charge is more localized and stronger hydrogen bonds can form between the surface oxygen and the interlayer water (Farmer, 1974). This different interlayer charge distribution, together with different hydration states, leads to physicochemical properties that depend on the type of smectite.

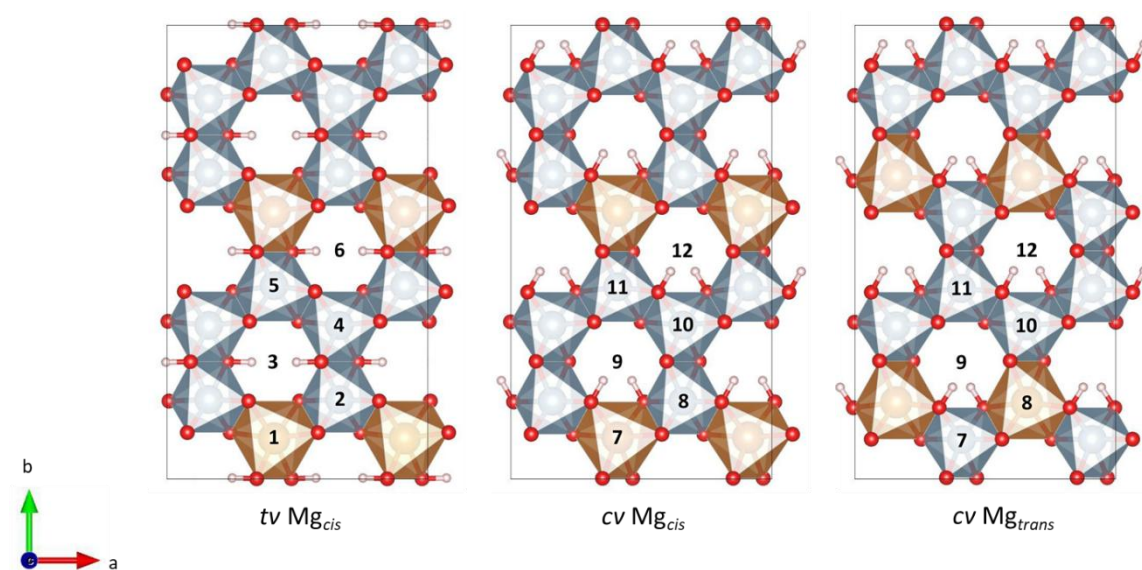


Figure 1.1: 2x2x1 supercells model octahedral sheet for $tv Mg_{cis}$, $cv Mg_{cis}$ and $cv Mg_{trans}$ with $\xi = 0.500$. White: hydrogen, red: oxygen, grey: aluminium, orange: magnesium.

The difference substitution position of Al^{3+} by Mg^{2+} in octahedral sheet resulted in three different structures. There are *trans-vacant* ($tv Mg_{cis}$), *cis-vacant1* ($cv Mg_{cis}$) dan *cis-vacant2* ($cv Mg_{trans}$). In these three structures, H^+ is added to complement the OH groups on the octahedral sheet. The oxygen atoms in octahedral sheet which bonded with added H^+ were chosen that the oxygen atoms are not bonded to silicon atoms in the tetrahedral sheet. The position of magnesium in the $tv Mg_{cis}$ structure is at octahedron position number 1, the position of magnesium in the $cv Mg_{cis}$ structure is at octahedron position number 7 and the position of magnesium in $cv Mg_{trans}$ is at octahedron position number 8 (Figure 1.1). The orientation direction of the OH group in the $tv Mg_{cis}$ structure is parallel to the a-axis,

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while in the $cv\text{ Mg}_{cis}$ and $cv\text{ Mg}_{trans}$ structures the orientation direction of the OH group is not parallel to the a-axis. The two of OH groups in $tv\text{ Mg}_{cis}$ and $cv\text{ Mg}_{cis}$ occupy the *cis*- position on the octahedron basic unit, while the two groups in $cv\text{ Mg}_{trans}$ occupy *trans*- position.

The overall net charge of the mineral layer influences the location and bonding of hydroxyl groups. The specific cation residing between the mineral layers also affects the orientation of the hydroxyl groups. The OH bond orientation in structural hydroxyl groups is influenced by both the layer charge (Mg-OH-Al bond number) and the interlayer cation type (Figure 1.2 and Figure 1.3). This orientation is defined by a polar angle (ρ), which is the angle between the OH vector and the (001) plane, and an azimuthal angle (ψ), which is the angle between the OH vector and the (010) plane (a mirror plane in the ideal $C2/m$ symmetry of the 2:1 layer). Due to this definition, the azimuthal angle (ψ) is always less than 90° . The OH bond's direction is not fixed but adjusts based on the chemical environment within the mineral. The polar and azimuthal angles (ρ and ψ) used as precise ways to describe this orientation. The restriction that $\psi < 90^\circ$ is a consequence of how the azimuthal angle is defined in relation to the specific mirror plane in these mineral structures.

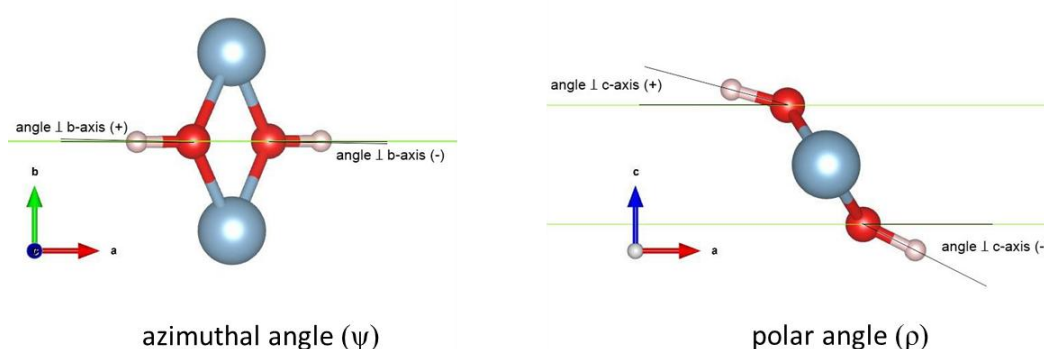


Figure 1.2: OH groups angle in $tv\text{ Mg}_{cis}$ structures

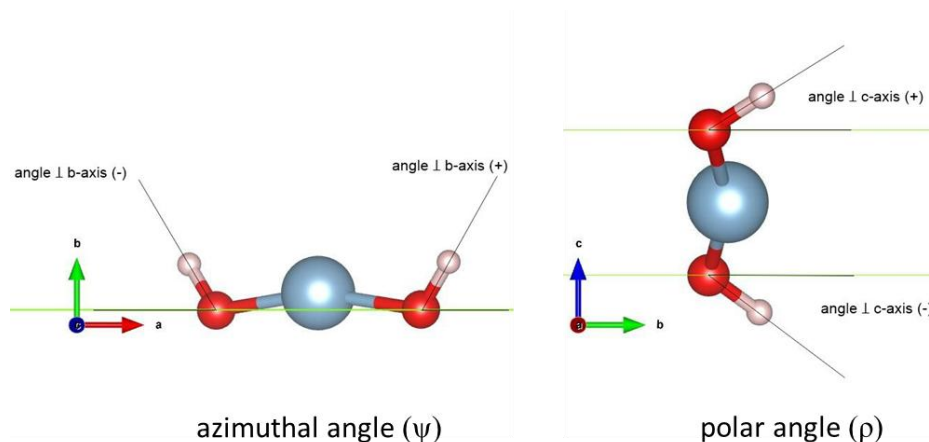


Figure 1.3: OH groups angle in $cv\text{ Mg}_{cis}$ and $cv\text{ Mg}_{trans}$ structures

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The distribution of aluminium and magnesium in octahedral sheets can be studied through laboratory experiments using spectroscopic analysis. Infrared spectroscopy is a tool that can be used effectively to determine the distribution, atomic arrangement and structural features in smectite structures. Besson and Drits (1997a, 1997b) suggested a new model to interpret the infrared spectra of dioctahedral mica in the OH-stretching region. It is based on the analysis of the main factors responsible for the observed sequence of OH frequencies. In terms of this model, the simple analysis depends on the OH frequency and the mass and valence of the cation bound to the OH group. The integrated optical densities of the OH bands were assumed to be proportional to the contents of the specific types of OH-linked cation pairs with the absorption coefficients being the same for all individual OH bands. Individual OH bands were assigned to specific cation pair types based on previous work without establishing any assignment rules. There have been significant uncertainties in the OH-band assignments (Madejova et al., 1992, 1994). Decomposition and curve-fitting of IR spectra applied to a representative collection of dioctahedral smectites provided a crystal-chemically consistent assignment of individual OH-stretching bands to specific types of OH bonded cation pairs (Zviagina, 2004).

Based on the structure and physicochemical properties of smectite, it has significant applications in various industrial sectors. Bentonite, which is naturally a rock composed mainly of smectite, is technically crucial and can be used in various industrial applications. Bentonite can be used as a pollution barrier from radioactive waste deposits, landfills and contaminated soils. Because bentonite has unique properties derived from its physicochemical properties, it is also used in various applications due to its absorption and adsorption properties to other substances such as the paint, paper, food, foundry, wastewater treatment, additives in detergents and paint litter industries. Smectite also has the ability to react with inorganic and organic polar compounds and also interact with water through hydration and dehydration processes, this is due to smectite's very small particle size, micro-sized pores, CEC and layer charge. The layer charge of smectite, the position of the charge layer and the layer dimension also affect the properties of swelling, high plasticity and rheological properties (Christidis et al., 2006; Christidis, 2008, Delavernhe et al., 2015). On the other hand, the distribution of octahedral cations in cis and trans positions affects the thermal stability of montmorillonite (Drits et al., 1995; Emmerich et al., 2009).

The dioctahedral type of smectite depends on the composition of the octahedral and tetrahedral sheets. Differences in thermal properties and thermal stability are attributed to their chemical composition (Schultz, 1969). Montmorillonite and the beidellite series are dioctahedral Al-rich smectites. Dioctahedral smectites are naturally intermediate in composition and are rarely found as montmorillonite or beidellite alone (Christidis, 2011). The Fe content in the montmorillonite-beidellite series also affects the physical and chemical properties and classification of the montmorillonite-beidellite series. Guggenheim et al. (2006) stated that if octahedral Al^{3+} exceeds Fe^{3+} , then the smectite is named as Fe^{3+} -rich beidellite or Fe^{3+} -rich montmorillonite. The substitution of Si^{4+} tetrahedral for Fe^{3+} is very rare in natural samples (Finck et al., 2019). Emmerich et al. (2009) added the configuration, cis or trans, as a new structural parameter required for the classification of dioctahedral smectites. The smectite structure reveals five features that allow an unambiguous description of a sample: 1) identification as either a dioctahedral or a trioctahedral smectite; 2) layer charge; 3) charge distribution between tetrahedral and octahedral sheets; 4) cation distribution within the octahedral sheet and 5) Fe content. In addition, the nature of interlayer cations should be given as they influence certain properties of montmorillonites (Emmerich et al., 2009).

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The octahedral sheet structure determines the thermal stability of the 2:1 phyllosilicate structure. The octahedral structure is related to thermal reactions that are useful for smectite applications in industry. Davidovits (1989) used aluminosilicate-based geopolymer materials as materials for storing toxic chemical or radioactive waste, making concrete, moulds for thermoplastic moulds and manufacturing of moulds. The thermal stability of bentonite determines their amount during the foundry process. These are research that examines the relationship between the octahedral structure and the physicochemical properties of smectites. These studies are related to the *cv* and *tv* structures to determine the formation mechanism of 2:1 dioctahedral smectites (Emmerich and Wolters, 2007). Moore (1997) analysed the structure of smectite using X-Ray Diffraction (XRD) but the 2:1 phyllosilicate structure shows structural defects, making it difficult to obtain precise structural information. Turbostratic disorder in smectite structure makes it difficult to identify the exact structure of smectite using XRD. Ufer et al. (2004) described the first acceptable description of XRD pattern of turbostratic disorder in smectite. Ufer et al. (2008) successfully performed phase quantification on smectite but did not intend to refine the structural details. Ufer et al. (2012) tried to refine the position of Fe occupancy in the octahedral position of illite-smectite intercalated minerals. However, the reliability of refinement decreased due to the high proportion of smectite layers. Some important structural features of Cu-trien-exchanged dioctahedral smectite such as LCD and octahedral iron content can be determined by Rietveld method and more structural information of turbostructurally disordered dioctahedral smectite can be obtained from X-ray powder diffraction patterns by Rietveld method (Wang et al., 2018).

Drits et al. (1998) state that *tv* smectite has a dehydroxylation temperature between 500 to 550 °C, and *cv* smectite has a dehydroxylation temperature of about 700 °C. Thermal analysis is a very effective method to improve the structure of octahedral sheets. Drits et al. (2006) considered that there was a compositional control on the distribution of octahedral cations over *trans*- and *cis*- sites in dioctahedral smectites. Wang et al. (2020) used the thermogravimetric (TG) analysis to characterize the structure of the octahedral sheet. The proportion of *cv* and *tv* configurations is calculated by fitting a derived differential thermogravimetric (DTG) curve that provides information of the dehydroxylation reaction at a given temperature when a water molecule exits the structure of each of the two OH groups. The dehydroxylation temperature of samples with *cv* configuration is about 680 °C and for samples with *tv* configuration is about 500 °C. Samples classified as *cv* varieties show a major dehydroxylation peak near 680 °C. On the other hand, samples classified as *tv* varieties show a major dehydroxylation peak between 450 and 500 °C. The content of *cv* and *tv* configurations depends on their chemical composition. The content of Fe³⁺ and Al³⁺ octahedral is strongly related to the proportion of *tv* and *cv* structures. With the increase of Fe³⁺ octahedral amount and the decrease of Al³⁺ octahedral amount, the proportion of *tv* increases.

1.3 Hydration of Smectite

The interaction between H₂O and 2:1 layered silicates in various forms has been studied using various experimental methods (Sposito and Prost, 1982; Sposito, 1984; Güven, 1992; Iwata et al., 1995; Schoonheydt and Johnston, 2013; Ferrage, 2016). Water can be bound in the interparticle space (pore water) and interlayer, forming a hydration layer with interlayer cations and interacting with the base surface. Weakly bound water can be released through drying under ambient conditions and has

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characteristics similar to bulk water (Sposito and Prost, 1982). The electric double layer forms a transition zone from the mineral surface to free pore water (Bourg et al., 2003; Bradbury and Baeyens, 2003; Kozaki et al., 2008; Tournassat and Appelo, 2011). The electric double layer contains cations, anions, and water, where excess cations neutralise the remaining charge on the outer surface of the particles. Emmerich et al. (2015) showed that the dielectric constant of water, or relative dielectric permeability, decreases with the number of H₂O molecules, and the attraction of the electric double layer at the mineral-water interface of clay mineral surfaces has been studied at the atomic scale, yielding detailed insights into how water reacts with these surfaces.

Interlayer water is strongly influenced by the structure of the 2:1 silicate layer (e.g., layer charge, charge location), the hydration properties of interlayer cations, and the particle size distribution that results in surface area. H₂O molecules at the interface are located between the silicate layers of the 2:1 layer and even have bidentate and monodentate orientations towards the solid surface (Szczerba et al., 2016). This structured water differs from pure water and its properties can extend several molecular diameters from the surface, highlighting its importance in understanding mineral surface chemistry. The ability of water molecules to reorient themselves and, as a result, influence chemical reactions near the interface. This suggests that the structure and physical properties of water near mineral surfaces can be very different from those of pure water, that surfaces can disrupt the structure and properties of fluids up to several molecular diameters from the surface, and that these differences are a key to understanding mineral surface chemistry (Kalinichev and Kirkpatrick, 2002; Bonaccorsi et al., 2004; Richardson, 2004; Korb et al., 2007; and Pellenq et al., 2008). Figures 1.4 illustrates the space available in unit cell (UC) that can be occupied by water molecules. The UC of montmorillonite has dimensions $a_0 = 5.17 \text{ \AA}$, $b_0 = 8.94 \text{ \AA}$, and $c_0 = 17.7 \text{ \AA}$ (Jasmund and Lagaly, 1993), while the diameter of a water molecule is $3 \text{ \AA}$. Therefore, the amount of water molecules per unit cell is 5.13.

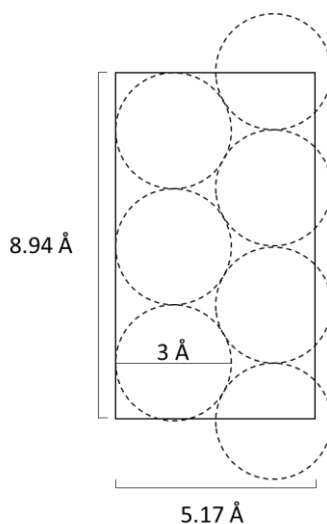


Figure 1.4: Space area occupied by water molecules per UC

Edge sorption sites on 2:1 layer silicates at higher pH are reactive due to their pH-dependent protonation and deprotonation, with deprotonated sites allowing cations to bind and form hydration shells, significantly influencing water distribution and overall reactivity. Understanding these sites is

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crucial because they contribute up to 10% of the CEC and are a key factor in the length scales of water interaction, from hydrogen bonding (< 0.35 nm) to internal crystalline swelling in smectite and vermiculite. The activity of these sites is determined by the pH, which dictates whether they are protonated (carrying a positive charge) or deprotonated (carrying a negative charge). When deprotonated, edge sites possess a negative charge, enabling them to bind cations from the surrounding water. The binding of cations to these sites can lead to the formation of a hydration shell, a layer of water molecules surrounding the ion. The pH of the environment, specifically in the 7–9 range for 2:1 layer silicates, significantly affects the number of deprotonated sites. This directly influences how water is structured and distributed within the material. Edge sorption sites contribute to the overall CEC, with one study showing a contribution of up to 10% (Delavernhe, et al., 2015). The smallest scale is the direct interaction of water molecules through hydrogen bonds, characterized by a bond length of less than 0.35 nm. A larger scale involves the gradual swelling of the crystal structure, as seen in minerals like smectite and vermiculite, driven by the uptake of water.

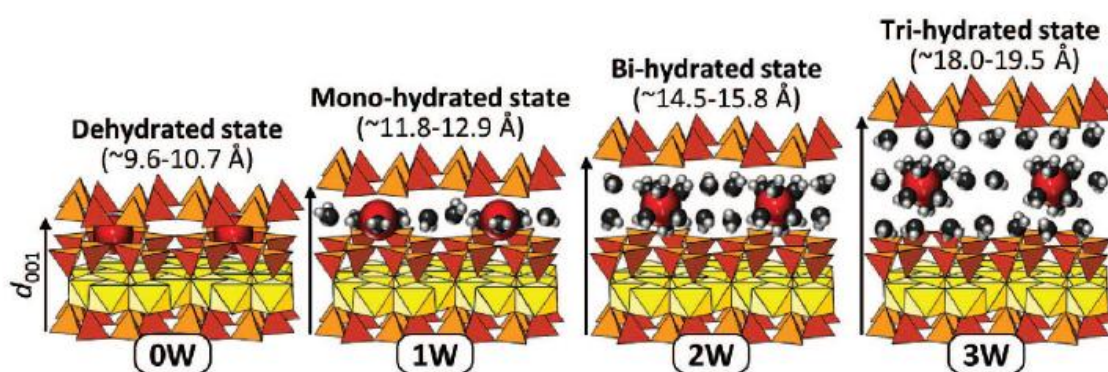


Figure 1.5: Hydration and crystalline swelling involves arrangement of water molecules in planes (Ferrage, 2016)

Crystalline swelling of smectite at low water content involves gradual expansion of interlayer spacing, forming discrete 1W, 2W, and 3W hydration states (mono-, bi-, and tri-hydrate) with increased basal spacing (d_{001}) observable XRD (Ferrage, 2016; Ferrage et al., 2011; Glaeser et al., 1967). These states, distinct from the dehydrated 0W state, represent water molecule intercalations between smectite layers. At distances beyond approximately 22 Å, crystalline swelling gives way to a dispersed double layer form due to interlayer cations, particularly with Na^+ and Li^+ , in smectite that is fully saturated with water. This process involves the intercalation of discrete layers of water molecules within the smectite's interlayer space. It occurs at low water contents and is characterized by the expansion of basal spacing. These are distinct levels of water intercalation, observable through XRD: 0W (Dehydrated): The base state with a layer thickness of approximately 9.6–10.7 Å. 1W (Mono-hydrated): One layer of water molecules, resulting in a thickness of about 11.6–12.9 Å. 2W (Bi-hydrated): Two layers of water, with a thickness of approximately 14.9–15.7 Å. 3W (Tri-hydrated): Three layers of water, leading to a thickness of roughly 18.0–19.0 Å.

This type of swelling occurs at higher water content or when smectite is saturated with interlayer cations like Na^+ and Li^+ . It is characterized by the dispersion of double layers between the smectite particles, with an associated d -spacing beyond 22 Å (Lagaly and Dékány, 2013). At low moisture levels, smectite undergoes crystalline swelling, gradually increasing its interlayer spacing as water molecules

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intercalate between the 2:1 layer. This intercalation proceeds through distinct states (0W, 1W, 2W, 3W), each with a specific increase in basal spacing. XRD is used to measure these increases in basal spacing, allowing researchers to identify the specific hydration states. When the amount of water is sufficient, especially in the presence of cations like Na^+ and Li^+ , the smectite layers become completely separated, leading to osmotic swelling.

XRD profile modelling, detailed in Ferrage et al. (2016), was used to quantify hydration states in smectites as a function of humidity and reveal the effect of layer charge. Higher layer charges result in decreased interlayer distances due to stronger electrostatic attraction between cations and layers, and cause the transition from bi-hydrated (2W) to mono-hydrated (1W) states to occur at lower relative humidity (r.h.) levels and water/cation ratios during dehydration. With increasing layer charge, the transition from the bi-hydrated (2W) state to the mono-hydrated (1W) state shifts to lower water content (specifically, lower $\text{H}_2\text{O}/\text{Na}^+$ ratios). This indicates that the higher charge allows the smectite to hold onto its water more strongly, requiring a drier environment for the dehydration transition to occur. The technique involves comparing experimental XRD patterns with calculated models of the smectite structure to determine the proportion of layers with different hydration states (e.g., 0W, 1W, 2W) at various r.h. Developed and applied the method to quantify the various hydration states as a function of r.h. (Ferrage et al., 2016). Used the modelling to study the effect of layer charge on interlayer water in natural dioctahedral smectites (Ferrage, et al., 2007). Applied XRD profile modelling to synthetic trioctahedral smectites (saponites) with tetrahedral charge to investigate the impact of charge location and level on hydration (Dazas, et al., 2015; Ferrage, et al., 2010a).

1.4 Computational Chemistry of Smectite

Computational modelling and simulation have become a promising method to investigate the microstructure of montmorillonite and its interlayer cation dynamics. Computational modelling also complemented experimental techniques by providing detailed insights that are often challenging to observe directly. Quantum Mechanics (QM) with ab initio thermodynamics calculation using DFT have been widely used to characterize the structure of montmorillonite and its properties. Quantum Mechanical Calculations enabled a comprehensive exploration of montmorillonite structure, hydration/dehydration dynamics, clay-fluid and clay layer-cations interactions. Computational simulation in our understanding of structure, dynamics, and energetics of layered materials: (1) the phenomenon of crystalline swelling is now well understood, thermodynamically stable layer hydrates have been identified; (2) cell parameters, and surface and interface energies of clay minerals can be computed in quantitative agreement with experiment; (3) self-assembly and dynamics of surfactants on clay mineral surfaces can be accurately simulated (Cygan et al., 2009).

Smectite hydration study using DFT is a relatively recent field that emerged after DFT became sufficiently accurate for quantum chemistry in the 1990s. The early development of DFT in the 1960s and 1970s laid the theoretical foundation, with first-principle, DFT-based calculations focusing on water-mineral interactions, including smectite, gaining prominence in the late 2010s and early 2020s. In general timeline of the key developments leading to the use of DFT for smectite hydration studies are: 1). Foundation of DFT (1960s–1970s) which the theoretical groundwork for DFT was established with the Hohenberg-Kohn theorems in 1964 and the Kohn-Sham approach in 1965, enabling the calculation of system properties from electron density; 2). Refinement of Foundation of DFT for

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Quantum Chemistry is Early Foundation of DFT applications were primarily in solid-state physics. Foundation of DFT methods became sufficiently accurate and versatile for quantum chemistry calculations, including studies of molecular interactions and adsorption, thanks to significant refinements in approximations for exchange and correlation functionals (1990s); 3). DFT-based methods for studying molecular-level interactions at mineral surfaces are increased use of first-principles. Specific studies began to apply DFT to analyse water molecule adsorption and the hydration mechanisms of smectite surfaces, especially, Application of DFT to Smectite Hydration; 4). Recent work includes DFT studies on hydration steps and the influence of interlayer cations and layer charge density on smectite hydration. For example, studies documented water adsorption mechanisms on sodium-montmorillonite surfaces and the interaction between hydrated smectite particles (late 2010s to early 2020s). (Berghout et al., 2010; Van Mourik et al. 2014; Liu et al., 2019; Peng et al., 2021; Min et al., 2022; Shen and Bourg, 2022).

Development of computational modelling in clay started with Na saturated montmorillonite models with 1 unit cell per supercell and layer charge $\xi = 0.5$ have been studied in dehydration state and with different water molecules in the interlayer using BLYP Functional with the result are 4 H₂O/Na⁺ by BYLP functional is 11.5 Å (Chatterjee et al, 2004). The dehydration models have the simulated basal spacing range from 9.6 - 10.1 Å, which is match the result of the natural dehydrated montmorillonite (Sainz-Diaz et al., 2005; Hernandez-Laguna et al., 2006; Voora et al., 2011; Shi et al., 2013, Emmerich et al., 2015; Li et al., 2016; Fonseca et al., 2017; Prasad et al., 2023). Hydrated appear to have basal spacing variation when different DFT function were implemented, for example, the basal spacing of models with 4 H₂O/Na⁺ in the interlayer range from 12 - 12.6 Å by PBE-based and PW91 functionals (Fonseca et al., 2017).

The simulation of water addition to the structural model can be seen from the results obtained in the form of the number of water molecules up to 7 H₂O/Na⁺, the basal spacing can reach to 14 Å or higher, which is in the transition stage of 1W to 2W state (Emmerich et al., 2015). The different layer charge of the montmorillonite model can also be comparison. Na saturated montmorillonite models with layer charge $\xi = 0.33$ have been studied, two research were applied PW91 functional but one of them was calculated without the dispersion corrections showed that when 4 H₂O/Na⁺ in the simulated model, the overestimation of basal spacing happened (Seppälä et al., 2016). Berghout et al. (2010) compared a 'dry' homoionic montmorillonite with water layer model of montmorillonite. The dry structured with divalent cation were found to have more compact and rigid structure than monovalent cation. Hydration results in expansion of the interlayer space. The type of cation also affects the hydrogen bonds formed between water molecules and basal oxygen atoms in montmorillonite layer.

Berghout et al. (2010) used First-principles calculations based on DFT were performed on the set of models with different levels of cation hydration with trans-vacant model of smectite, and the results that the dry structures with divalent cations were found to have more compact and rigid structures than structures with monovalent cations and d001 values did not change regularly with increasing ionic radius in the dry structures. Different of cation radii also effect to interaction between a negative layer and cation, attraction a negative layer charge to larger cation radii less than to smaller cation radii. Smaller cations radii are tended to located close the basal oxygen atoms of trigonal holes, while larger cations are located relatively symmetrically in interlayer, The Na saturated montmorillonite model with 2 unit cells per supercell and layer charge $\xi \leq 0.25$ was first calculated from the research of Berghout et al by PW92 functional, it showed that when 4 and 6 H₂O/Na⁺ were added into the

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structure, the basal spacing are 12.43 and 12.53 Å which are close to the available experimental results. other research from Emmerich et al presented similar results by PW91 functional (Emmerich et al., 2018).

Lavikainen et al. (2015 and 2016) studied DFT modelling of dioctahedral smectite using a model supercell representing a fully periodic smectite particle was generated from a trans-vacant pyrophyllite unit cell. The cleavage edge faces were hydroxylated and protonated to be formally neutral with variable proton configuration. The structural deformation due to the Mg and Al substitution and the surface electrostatic potential was observed to be most negative near the octahedral Mg-substitution. The structural deformation due to the Mg and Al substitution. The presence of water molecules in the smectite structure have been an interesting investigation in several research. Chatterjee et al., (1999) are studied the first attempt to generate a realistic model (with DFT) for clay-cation-water system using a model 2:1 dioctahedral smectites (montmorillonite and beidellite). The results showed that the interlayer cation Na⁺ is surrounded by five water molecules and the cation located near to the surface and the adsorption energy for montmorillonite more stable than beidellite. Emmerich et al., (2018) investigated water content and hydration behaviour of dioctahedral smectite based on structural and morphological properties. Layer charge distribution reduce basal spacing. Montmorillonite and beidellite with layer charge 0.125 are swellable. To improves the accuracy of DFT calculation, some research using PW91 functional or PBE functional. In this study, we are using the DFT-D3 functional which is a latest version of DFT calculation with correction to van der Waals forces. The DFT-D3 method is used as a more advance method to explain structural and energetic aspects that focused on the interaction of Van der Waals forces and hydrogen-bonded water molecules. Since The use of DFT-D3 methods aim to obtain accurate results regarding the mobility of interlayer cation in the presence of water molecules (Grimme et al, 2010 and 2011).

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2 Methods

2.1 Density Functional Theory Calculation

2.1.1 Model Structure

The basic montmorillonite structure was obtained from the montmorillonite structure recommended by Tsipursky and Drits (Tsipursky and Drits, 1984). The position of each atom in this structure is in three-dimensional space coordinates with the following unit cell sizes: $a_0 = 5.18 \text{ \AA}$; $b_0 = 8.98 \text{ \AA}$; and $c_0 = 10.05 \text{ \AA}$, with a monoclinic crystal structure system with C 2/m symmetry. All angles are equal to 90° for simplification. OH groups added in octahedral sheet and substitution of Mg^{2+} to substitution Al^{3+} with different position resulted $tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ structures.

2.1.2 Optimization of Homoionic Saturated Montmorillonite Structures

The cations in the interlayer were then adjusted to the desired montmorillonite structure and studied in this study: Na^+ , K^+ , Ca^{2+} and Mg^{2+} -saturated montmorillonite. The simple structure used as starting model, $1 \times 1 \times 1$ cell model for monovalent cation and $2 \times 1 \times 1$ cell model for divalent cation. The optimization of each structure was carried out in the absence of water molecules in the interlayer. Determination of the position of interlayer cation in the input file is done by dividing the cross-sectional area from the c-axis direction in unit cell.

The effect of cation type in the interlayer on the structure and properties of homoionic saturated montmorillonite was studied by performing duplication of the $1 \times 1 \times 1$ (Na^+ and K^+ -saturated montmorillonite) and $2 \times 1 \times 1$ (Ca^{2+} and Mg^{2+} -saturated montmorillonite) cell model into a supercell model for different layer charges. Duplication produced supercell models with layer charge 0.250 and 0.500, while the duplication of four-unit cells (Na^+ and K^+ -saturated montmorillonite) and eight-unit cells (Ca^{2+} and Mg^{2+} -saturated montmorillonite) produced supercell models with layer charge 0.125 and 0.375. The convergence of the atomic configuration of each type of structure ($tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$) with different layer charge ($\xi = 0.125, 0.250, 0.375$ and 0.500) is tested by performing a series of calculations with different layer thickness (c). The minimum thermodynamic parameters are determined by solving the Birch-Murnaghan equation of state.

This method was used not only to determine the effect of interlayer cation type on basal spacing changes, but also to determine the properties of anhydrous homoionic saturated montmorillonite, such as specific density variations, layer thickness, position of interlayer cations, interlayer thickness, oh vectors orientation, elastic properties, and bulk modulus.

2.1.3 Total Energy Distribution

The Total Energy (eV) distribution of each structure was determined through a series of calculation by placing the cation at different position in interlayer. The Total Energy was calculated for all octahedral sheet structure models (*tv Mg_{cis}*, *cv Mg_{cis}* and *cv Mg_{trans}*). This study is limited to the simplest structure of each structure (1UC for monovalent cations and 2 UC for divalent cations, each with $\xi = 0.500$). This series of calculation is also used to determine the most stable structure with the exact position of cation. The most stable structure is indicated by the lowest Total Energy (eV). The ionic mobility of cation in each homoionic saturated montmorillonite structure was determined by first determining the specific point occupied by cation in the Total Energy distribution. These points indicate the position of the cation with the highest structural stability in the area that can be occupied by cation with high probability and stability. These points are then connected to another point with the same condition in next unit cell to make a pathway. Water molecules were added into structures (only Na⁺ and K⁺-homoionic saturated montmorillonite) to further investigate of ionic mobility. The addition of water molecules is intended to determine the effect of hydrated ion to ionic mobility which compared with ionic mobility in structures without water molecules.

2.1.4 Hydration of Homoionic Saturated Montmorillonite

The hydration modelling of montmorillonite was continued by adding water molecules (0, 2, 4, 6 and 8 water molecules per cation) in layer charge 0.250 and 0.500 to the most stable structure which obtained from section 2.1.2. Hydration of homoionic saturated montmorillonite was calculated for all octahedral sheet structure models (*tv Mg_{cis}*, *cv Mg_{cis}* and *cv Mg_{trans}*). This research models montmorillonite behaviour at various water contents by adjusting layer thickness and uses the Birch-Murnaghan equation to find the most stable state. The study focuses on the stable water configurations, how layers expand, and the amount of water in Na⁺, K⁺, Ca²⁺, and Mg²⁺-saturated montmorillonite, extending the work of Emmerich, et al. (2018).

2.1.5 Computational Chemistry Method

The electronic structure, atomic geometry, and total energy of montmorillonite models were calculated by DFT. Functional Generalized Gradient Approximation Perdew-Burke-Ernzerhof (GGA-PBE) (Perdew, et al., 1996; Perdew, et al., 1997) and Projector Augmented Wave (PAW) methods for electron-ion interaction (Kresse and Joubert, 1999) were used as implemented in the Vienna Ab Initio simulation package (Kresse and Hafner, 1993; Kresse and Hafner, 1994; Kresse and Furthmüller, 1996; Stadler, et al., 1996). The valence electrons used for each atom are 3s² 3p² for Si, 3s² 3p¹ for Al, 3s² for Mg, 3s¹ for Na, 4s¹ for K, 2s² 2p⁴ for O, and 1s¹ for H. VASP.5.3.4 version was used in this study. Van der Waals correction (dispersion): IVDW = 12 (DFT-D3 method with Becke-Johnson damping function). The valence electron function is extended in-plane up to a kinetic energy limit of 400 eV. Brillouin zone sampling was performed with 1 x 1 x 1 mesh from the Monkhorst-Pack k-point.

Visualization for structural models, volumetric data such as electron/nuclear density, and crystal morphology using Visualization for Electronic and Structural Analysis (VESTA), where the atomic radii are 1.18 Å for Si, 1.43 Å for Al, 0.74 Å for O, Å and 0.46 Å for H; and the ionic radii are 1.02 Å for Na, 1.51 Å for K, 1.12 for Ca and 0.72 Å for Mg.

Optimization of unit cells size, unit cell shape and atomic coordinates was performed via a conjugate gradient technique for the bulk materials. This technique utilized the Total Energy in eV and the Hellman Feynman forces on the atoms and stresses on unit cell. The convergence in calculation of clay minerals is also dependent on the thickness of the mineral layer and the thickness between the layers. The convergence checked by running a series of calculations with different layer thicknesses for every atomic configuration and the thermodynamic minimum was then constructed by solving the Birch–Murnaghan equation of state (Emmerich, et al., 2018; Berghout, et al., 2010).

2.2 Homoionic Exchange

The preparation of homoionic exchange samples follows the methodology described in the study by Steudel and Emmerich (2013). As mentioned in the literature, there is a simple protocol regarding the concentration of the exchange solution for the preparation of homoionic smectite from natural samples. The success of homoionic exchange is influenced by various factors, including the properties of smectite, the initial cation in the interlayer, the soluble phase in the initial material, sample pre-treatment, and experimental setup. The properties of smectite and cations are greatly influenced by the soluble phase. Therefore, the following two things are necessary before exchange: mechanical pre-treatment of the sample by dispersing the raw material and separating the clay fractions through sedimentation; and chemical pre-treatment and ‘initial opening’ of the interlayer.

The homoionic exchange process includes the removal of carbonates, washing with NaCl and deionized water, separation of the <2 μm fraction, saturation with Na^+ , K^+ , and Ca^{2+} , and Mg^{2+} the dialysis process.

2.2.1 Materials

The materials used in this study were Calcigel from Bavaria (Clariant) and Secursol UHP from Westerwald (Stephan Schmidt KG). Calcigel and Secursol UHP are the commercial names of bentonites. Calcigel from Moosburg area (Landshut region, Bavaria) Germany is a Ca/Mg-bentonite that has been studied and used for various geotechnical applications, particularly as a potential buffer material in the German multi-barrier concept for the disposal of high-level waste. Secursol UHP is a high-purity, high-swelling Westerwald bentonite clay from Germany, used as a sealing material in underground waste repositories due to its excellent hydraulic sealing and swelling properties mined from three open pits (Arborn, Ruppach, and Salz) in Ruppach-Goldhausen (Westerwald region) Germany. Characterized by a very high swelling pressure, it is a highly plastic clay composed of montmorillonitic beidellite smectite and is used in granular or pillow forms for geotechnical applications, such as in sandwich sealing systems (Emmerich et al., 2021; Wieczorek et al., 2024; Asaad et al., 2025).

As investigated and reported by Asaad et al. (2025), Calcigel and Secursol UHP have the following characteristics: Calcigel and Secursol UHP are confirmed as Ca/Mg-bentonite with similar main mineralogical phases but different proportions. Calcigel and Secursol UHP contain pure dioctahedral smectite phases. Secursol UHP has a 20% higher smectite content. The smectite in Secursol UHP has a Ca:Mg ratio approximately 45% higher than Calcigel. This smectite also exhibits a higher layer charge, more Fe content, and less Al content in its octahedral sheets, as well as a slightly higher Mg content (0.33 vs 0.31), resulting in a slightly higher specific density of smectite in Secursol UHP. Based on AFM data on a single smectite layer, the average equivalent disk diameter of Calcigel is 25% larger than that of Secursol UHP, with a slightly higher average layer stacking in powder form (9 layers vs 8 layers for

Secursol UHP). Meanwhile, Secursol UHP shows a slightly wider smectite particle size distribution. For both Calcigel and Secursol UHP, the water content (from air-dried material) measured at 105 °C was approximately 20% (relative) lower than that measured at 200 °C, indicating that the material remained in its first hydration state after drying at 105 °C. The minor mineral phase content, particle morphology, size distribution, and chemical composition of the smectite phase all indicate that Secursol UHP was formed under more stable physicochemical conditions than Calcigel.

2.2.2 Chemicals

The chemicals used are as follows: Acetic Acid (CH_3COOH , Rotipuran® 100% p.a., Carl Roth GmbH & Co KG Germany), Calcium Chloride (CaCl_2 , Reag. Ph Eur, Merck KGaA Germany), Deionized Water, Ethyl Alcohol ($\text{C}_2\text{H}_5\text{OH}$, absolute pure, PanReac AppliChem ITW Reagents Germany), Lithium Bromide (LiBr , $\geq 99\%$ water free, Carl Roth GmbH & Co KG Germany), Lithium Chloride (LiCl , purified, VWR Chemicals Germany), Lithium Iodide Trihydrate ($\text{LiI} \cdot 3\text{H}_2\text{O}$, $\geq 99\%$ extra pure, Carl Roth GmbH & Co KG Germany), Magnesium Chloride Hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 99% p.a., Haberle Labortechnik GmbH & Co KG Germany), Magnesium Nitrate Hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Reag. USP. Ph Eur, PanReac AppliChem ITW Reagents Germany), Potassium Acetate (KCH_3CO_2 , extra pure Ph Eur, Merck KGaA Germany), Potassium Carbonate (K_2CO_3 , 99% p.a., Carl Roth GmbH & Co KG Germany), Potassium Chloride (KCl , extra pure, Merck KGaA Germany), Potassium Sulphate (K_2SO_4 , p.a., Merck KGaA Germany), Silica Gel (2-5 mm, Perlform, Carl Roth GmbH & Co KG Germany), Sodium Acetate Trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, rectapure, VWR Chemicals Germany), Sodium Bromide (NaBr , 99% p.a., Carl Roth GmbH & Co KG Germany), Sodium Chloride (NaCl , 99.5% p.a., Carl Roth GmbH & Co KG Germany), Sodium Dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), Sodium Hydrogen Carbonate (NaHCO_3 , $\geq 99\%$, p.a., Carl Roth GmbH & Co KG Germany), Silver Nitrate (AgNO_3 , p.a. Reag. Ph Eur, PanReac AppliChem ITW Reagents Germany), Trisodium Citrate Dihydrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 3\text{H}_2\text{O}$, $\geq 99\%$, p.a., Carl Roth GmbH & Co KG Germany).

2.2.3 Equipment

The equipment used are as follows: Agate mortar, Beaker, Centrifuge (Multifuge 3 S-R Heraeus), Centrifuge tube, Porcelain bowl, Conductometer (WTW 11460296), Dialysis tubes (Nadir, pore size 25A), Hygrometer (Klima@home Funk-Thermo-Hygrometer TFA), Magnetic stirrer (IKA®C-MAG HS7), Measuring cylinder, Measuring flask, Molecular sieve $<200 \mu\text{m}$ (Retsch GmbH & Co), Oven (Heraeus Instrument Type T6120 and Thermo Scientific Heraeus Type UT20), Peleus ball, pH meter, pH universal stick (Merck Germany), Rotating centrifuge tube, Scales (Mettler AE 200s, Mettler Toledo MS603TS/00 and Sartorius Weighing Technology GmbH), Shaker (Swip SM25), Sonicator (Retsch GmbH & Co KG type USG.110475), Timer, Ultrasonicator (Ultraschallprozessor UP 200s dr. hieslscher GmbH), U-shaped glass tubes, UV Visible spectrophotometer (Genesis 10 UV Thermo Electron Corporation), Water jet pump, sample storage box.

2.2.4 Removal Carbonates

The carbonate removal procedure for the Calcigel and Secursol UHP samples follows the sequence described below. Acetate buffer was prepared by mixing 2 M $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (aq) with 2 M CH_3COOH (aq) at a ratio of CH_3COONa (aq): CH_3COOH (aq) is 2:1. The concentrated acetic acid (CH_3COOH , Rotipuran® 100% p.a., Carl Roth GmbH & Co KG Germany) used has a concentration of 17.5 M, and to prepare 1 L CH_3COOH (aq) with liquid concentration 2M needed 114 mL of concentrated acetic acid (CH_3COOH , Rotipuran® 100% p.a., Carl Roth GmbH & Co KG Germany) diluted to one litre of deionized

water. 2 M $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (aq) prepared by dissolved 544.32 g Sodium Acetate Trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, rectapure, VWR Chemicals Germany) diluted to two liters deionized water. 2 L $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (aq) 2 M and 1 L CH_3COOH (aq) 2 M mixed and stirred for 15 minutes. The acetic buffer has a pH of 4.8 measured with pH universal stick (Merck Germany).

One hundred gram of each sample were put into beaker. Samples are Calcigel (Clariant) and Secursol UHP (Stephan Schmidt KG), both samples were prepared as much as 400 g each, and each 100 g was prepared for homoionic sample preparation (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). 1000 ml Acetate buffer added into a 3-liter beaker which already contained samples. The ratio of sample solids to acetate buffer solution was 100 g: 1000 ml. After the acetate buffer was mixed with the solid sample, CO_2 bubbles were formed. The suspension was stirred using Magnetic stirrer (IKA®C-MAG HS7) for 5 hours at room temperature and without heating.

The CO_2 bubbles produced from the Calcigel (Clariant) sample were more than the Secursol UHP (Stephan Schmidt KG) sample. After 5 hours of stirring, the suspension was settled overnight. After settling overnight, the supernatant was separated from the solids using a U-shaped pipe and discarded. The process was repeated by adding a new fresh 1000 ml acetate buffer, stirring for 5 hours, suspension settled overnight, supernatant separated, and discarded. This repetition aims to ensure that no more CO_2 gas bubbles are formed.

2.2.5 Washing by NaCl and Deionized Water

One litre of Sodium Chloride (NaCl , 99.5% p.a., Carl Roth GmbH & Co KG Germany) (aq) 1 M added to the beaker with the carbonate-free solid. Suspension stirred for 2 hours then allow the suspension to coagulate for a few hours. More salt is added to coagulate. 58.44 g Sodium Chloride (NaCl , 99.5% p.a., Carl Roth GmbH & Co KG Germany) solid added to the beaker and stirred for 2 hours, then allow the suspension to coagulate for a few hours. Coagulation was not observed. Sodium Chloride (NaCl , 99.5% p.a., Carl Roth GmbH & Co KG Germany) solid in steps of 1 Mol (with subsequent stirring) was added until the suspension contained 6 Mol Sodium Chloride (NaCl , 99.5% p.a., Carl Roth GmbH & Co KG Germany) to make sure the sample are completely coagulated. Total mass of Sodium Chloride (NaCl , 99.5% p.a., Carl Roth GmbH & Co KG Germany) added are 350.64 gram for each sample. The amount of salt added is equivalent to 98 times CEC Calcigel (Clariant) and 68 times CEC Secursol UHP (Stephan Schmidt KG) (CEC of Calcigel (Clariant) = 61 cmol (+)/kg; and CEC of Secursol UHP (Stephan Schmidt KG) = 88 cmol (+)/kg).

Supernatant was siphoned and the sample was transferred with about 400-500 ml deionized water into 600 ml centrifugation bottles, then centrifuged for 30 minutes at 4500 rpm using Centrifuge (Multifuge 3 S-R Heraeus). Supernatant was decanted. Deionized water was added to 600 ml centrifugation bottles (approximately 400-500 ml). Suspension re-dispersed by shaking and sonication. Sonication using rod sonicator (Retsch GmbH & Co KG type USG.110475) for 15 minutes.

The suspension centrifuged using Centrifuge (Multifuge 3 S-R Heraeus) for 30 minutes at 4500 rpm and removed the supernatant (decanted). The addition of deionized water was repeated until the centrifuge supernatant was not clear and this happened with the fourth repetition of adding deionized water.

2.2.6 Separation of <2 μm Fraction

Dispersion transferred into 5 L beakers with deionized water. Sample dispersed in deionized water. Suspension stirred using Magnetic stirrer (IKA®C-MAG HS7) for 30 minutes for homogenization. For extraction of the < 2 μm fraction in 5 L beakers, the sedimentation distance was set to 20 cm, specific density of quartz was used (2.66 g/cm³) following Stokes' law. For a room temperature of 20°C (temperature-controlled lab), the settling time is 15 h 24 min. The sedimentation process was carried out at room temperature of 20 °C. After the sedimentation process is complete, the sediment (fraction > 2 μm) and suspension (fraction < 2 μm) are separated using a U-shaped pipe. The fraction < 2 μm siphoned from a beaker stored in a bucket. The steps (dispersed, stirred, settled, and siphoned) are repeated four times. At the end of the sedimentation process, ~16 litres of < 2 μm fraction was obtained. The sediment was dried at 60 °C in oven (Heraeus Instrument Type T6120).

2.2.7 Saturated with Na⁺, K⁺, Ca²⁺ and Mg²⁺

Each Suspension was coagulated with different salt [Sodium Chloride (NaCl, 99.5% p.a., Carl Roth GmbH & Co KG Germany); Potassium Chloride (KCl, extra pure, Merck KGaA Germany); Calcium Chloride (CaCl₂, Reag. Ph Eur, Merck KGaA Germany) and Magnesium Chloride Hexahydrate (MgCl₂.6H₂O, 99% p.a, Haberle Labortechnik GmbH & Co KG Germany)]. Adding the mass of the salt corresponding to 50 times CEC for monovalent cations or 20 times CEC for divalent cations. Assuming that the mass of the extracted < 2 μm fraction is ~85 g and the CEC of the < 2 μm is ~100 cmol (+)/kg. The exchange and coagulation process were carried out by adding salt to each suspension (fraction < 2 μm) to reduce the volume. The addition of salt is carried out little by little until the total mass corresponds to 50 times CEC for monovalent cations or 20 times CEC for divalent cations. The clear supernatant siphoned and transferred to four 600 ml centrifugation bottles, then centrifuged for 30 minutes at 4500 rpm using Centrifuge (Multifuge 3 S-R Heraeus), and remove the clear supernatant. For KCl, CaCl₂, MgCl₂.6H₂O 2 or 3 more times of 50 times (K) and 20 times (Ca or Mg) CEC has to be added/stirred/centrifuged. Re-dispersed the sample with deionized water by sonication (rod sonicator, Retsch GmbH & Co KG type USG.110475) until the supernatant is not clear.

2.2.8 Dialysis Process

The dialysis tube (Nadir, pore size 25A) is immersed in boiling water for 4 hours. This process is repeated 2 times. Sample is put into the dialysis tube. During the dialysis process, demineralized water was changed daily. Conductivity is monitored using Conductometer (WTW 11460296). Dialysis was carried out until the conductivity of the demineralized water was less than 5 $\mu\text{S}/\text{cm}$, and Chloride free solution can be confirmed by the AgNO₃ test [Silver Nitrate (AgNO₃, p.a. Reag. Ph Eur, PanReac AppliChem ITW Reagents Germany)]. After completion of dialysis, the samples were dried at 60 °C in oven (Heraeus Instrument Type T6120). After drying, the samples were crushed gently using an agate mortar.

2.3 Water Adsorption on Homoionic Saturated Montmorillonite

2.3.1 Relative Humidity Sample Preparation

A 5-litre sample storage box with a tight-fitting lid is prepared. Petri dishes with a diameter of 11.5 cm are prepared for storing saturated salt solutions, and petri dishes with a diameter of 6 cm are prepared for storing samples, illustrated in figure 2.1.

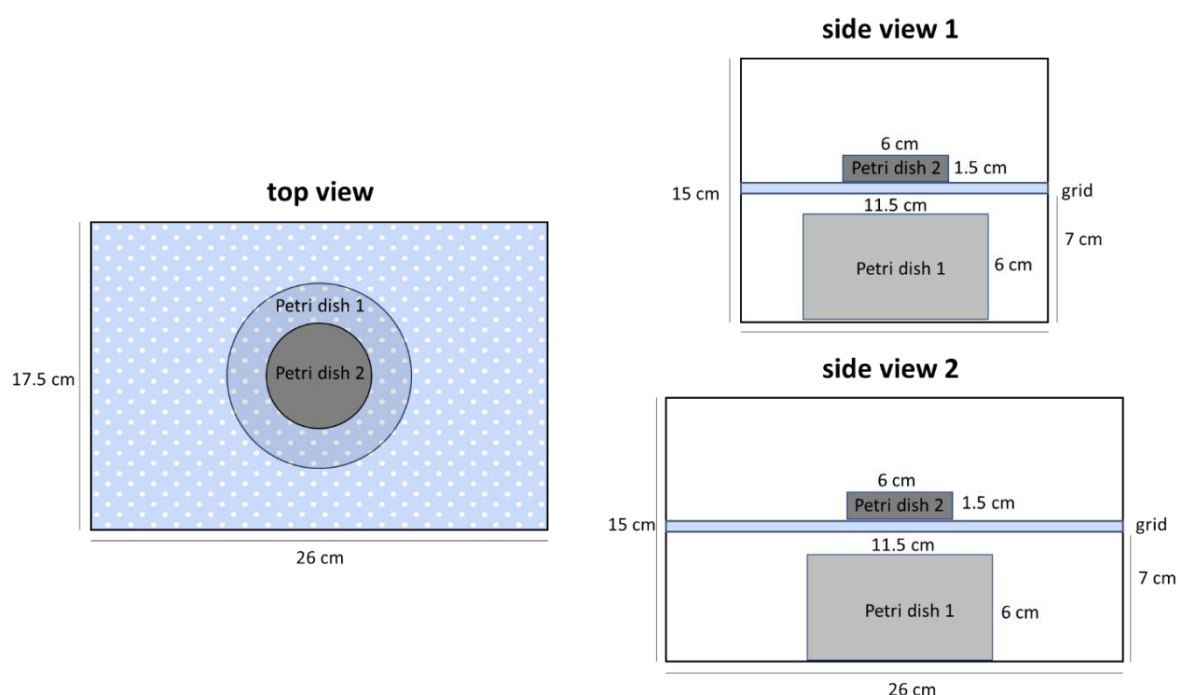


Figure 2.1: Sample storage box sketch

Saturated salt solutions with a specific r.h. (Table 2.1) are prepared by dissolving the salt solids in deionised water. The salts were used as follow: Lithium Bromide (LiBr, $\geq 99\%$ water free, Carl Roth GmbH & Co KG Germany), Lithium Chloride (LiCl, purified, VWR Chemicals Germany), Lithium Iodide Trihydrate ($\text{LiI} \cdot 3\text{H}_2\text{O}$, $\geq 99\%$ extra pure, Carl Roth GmbH & Co KG Germany), Potassium Acetate (KCH_3CO_2 , extra pure Ph Eur, Merck KGaA Germany), Magnesium Chloride Hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 99% p.a, Haberle Labortechnik GmbH & Co KG Germany), Potassium Carbonate (K_2CO_3 , 99% p.a, Carl Roth GmbH & Co KG Germany), Magnesium Nitrate Hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Reag. USP. Ph Eur, PanReac AppliChem ITW Reagents Germany), Sodium Bromide (NaBr, 99% p.a., Carl Roth GmbH & Co KG Germany), Sodium Chloride (NaCl, 99.5% p.a., Carl Roth GmbH & Co KG Germany), Potassium Chloride (KCl, extra pure, Merck KGaA Germany) and Potassium Sulphate (K_2SO_4 , p.a., Merck KGaA Germany).

Each salt is weighed with a different mass according to its solubility, then the salt is dissolved in deionised water little by little until the salt solid no longer dissolves. The saturated salt solution is placed in a separate storage box that has been labelled according to the r.h. mentioned earlier. A

hygrometer (Klima@home Funk-Thermo-Hygrometer TFA) is placed inside the storage box to monitor the r.h. value. The storage box is then stored for at least 24 hours or until the r.h. inside the box is constant in a room with a temperature of 20 °C for at least 24 hours before the sample is ready to be placed in the storage box.

Table 2.1: r.h. and salt solubility in water

Salt	r.h. [%] in 20 °C (Greenspan, 1977)	Solubility in 100 g of water		Measured per 100 ml deionized water
		20 °C	25 °C	
Silica gel	0			
LiBr	6.61 ± 0.58	143 g	181 g	181.54 g
LiCl	11.31 ± 0.31	83.5 g	84.5 g	84.75 g
LiI.3H ₂ O	18.56 ± 0.16	133.84 g	165 g	165.87 g
KCH ₃ CO ₂	23.11 ± 0.25	256 g	268.6 g	268.78 g
MgCl ₂ .6H ₂ O	33.07 ± 0.18	54.9 g	56 g	56.45 g
K ₂ CO ₃	43.16 ± 0.33	110.3 g	111 g	111.25 g
Mg (NO ₃) ₂	54.38 ± 0.23	42 g	71.2 g	71.36 g
NaBr	59.14 ± 0.44	90.5 g	94.6 g	94.70 g
NaCl	75.47 ± 0.14	35.8 g	36 g	36.21 g
KCl	85.11 ± 0.29	34.7 g	35.5 g	35.41 g
K ₂ SO ₄	97.59 ± 0.45	11.1 g	12 g	12.22 g

2.3.2 Water Adsorption

Two hundred milligrams of air-dry samples put in glass placed in storage boxes with specific r.h. levels. Samples prepared in triple measured. The sample masses were monitored periodically at specific intervals. Sample measurements were completed once stable masses were obtained and no increase or decrease in sample mass occurred (it takes an average of one week). The sample mass was measured using a Mettler AE 200s balance. After the constant mass was obtained, the samples were then dried with drying times varying between 24 hours and 48 hours, and temperatures varying between 105 and 200 °C in oven (Thermo Scientific Heraeus Type UT20).

2.4 Analytical Methods

2.4.1 X-Ray Diffraction Analysis (XRD)

XRD was used to quantifies the effect of water on interlayer spacing by measuring Bragg reflection. The method is based on the diffraction X-rays by crystal structure. The diffraction can be described by Bragg's law.

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$$

n = natural number indicating the diffraction order; λ = wavelength of X-rays (Å); d = lattice spacing; θ = diffraction angle (°)

This allows for the determination of basal spacing and amount of water in the interlayer at different r.h. The samples are subjected to controlled changes in relative humidity, from high r.h. to vacuum conditions. XRD experiments are conducted in situ, meaning the diffraction is measured while the material is under the varying r.h. conditions. The study of hydration and dehydration as a function of r.h. can reveal hysteresis, where the water content and basal spacing depend on the direction of the hydration cycle, offering information about water-material interactions.

2.4.2 Cation Exchange Capacity (CEC) Measurement

The CEC determination for raw material and homoionic saturation samples followed the copper-triethylenetetramine (Cu-Trien) method CEC (Meier & Kahr, 1999). 15 mL centrifuge tubes were used to mix 50 mg of the powdered sample with 10 mL deionized water and 5 mL of a 0.01 mol/L copper-triethylenetetramine (Cu-Trien) solution. The sample was shaken by hand briefly and, subsequently, placed on a shaking table (Swip SM25) for 3 h. Afterwards, the sample was centrifuged at 4500 rpm (4347xg) for 10 min (Heraeus Multifuge 3 S-R, Thermo Heraeus, Thermo Fisher Scientific Inc., Massachusetts, USA). A UV-Vis spectrophotometer (Genesys 10 UV, Thermo Electron Corporation, Massachusetts, USA) was used at a wavelength (λ) of 580 nm to measure the absorbance of the supernatants using polystyrene microcuvettes (path length 1 cm; Lab Logistics Groups GmbH, Germany). The concentration of Cu-Trien of the supernatants was determined by a calibration curve. By the depletion of the supernatant due to the exchange of interlayer cations by Cu-Trien the CEC [cmol (+)/kg] was calculated. Subsequently to CEC measurements, the exchanged cations in the sample solution were determined. For Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) measurements, 5 ml of the solution from CEC experiment were diluted in the 1:1 ratio by 5 ml deionized water and acidified with 0.25 ml 1 M HNO₃. Then the concentration of cations (in mg/L) which were exchanged (e.g., Na⁺, K⁺, Ca²⁺, Mg²⁺) were determined by ICP-OES. A recalculate and verification of the measured CEC can be done according to the total amount of exchanged cations.

2.4.3 Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

ICP-OES was utilized to measure the concentrations of exchanged cations in the supernatant solution. This process involves vaporizing the solution and introducing it into an argon plasma, elevating temperatures to 5000 - 7000 K and converting it into an aerosol. Under such high temperatures, elements become ionized and subsequently excited, emitting characteristic wavelengths of light pulses that can be precisely measured as a means of analysis. The ICP-OES was carried out with an Optima 8300DV (PerkinElmer, Massachusetts, USA). Liquid samples from solubility experiments were acidified and diluted according to a measuring range of Si and Al concentrations in solution of 30 mg/L. The exchanged cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) of the clay minerals were also analysed by ICP-OES, the sample preparation was conducted according to the description in chapter 3.2. By this analysis the ratio of the exchanged cations relative to each other could be determined.

Table 2.2: Characteristic wavelengths of main analysed cations

Cation	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Al ³⁺	Si ⁴⁺
Wavelength (nm)	589.529	766.491	279.553	396.847	396.153	251.611

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3 Effect of Different Cation in Interlayer (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) on Homoionic Saturated Montmorillonite Structures and its Properties

Part of this chapter is submitted for publication.

3.1 Introduction

Montmorillonite, member of the smectite clay mineral group, has received extensive attention due to its unique structural, physicochemical, and swelling properties. Its ability to intercalate water molecules and exchange cation within its interlayer space make it a model system for studying clay-water and clay-cation interaction. These properties are fundamental for various applications, including environmental remediation, catalysis, drilling fluid, and engineered barriers for waste containment. Understanding the atomic-scale mechanism governing these processes requires an accurate and detailed description of montmorillonite's structure and energetics (Teich-McGoldrick et al., 2015; Yaghmaeiyan et al., 2022; Uddin et al., 2024).

In recent decades, Quantum mechanical calculations and computational simulations have significantly advanced the understanding of montmorillonite, enabling accurate simulations of its crystalline swelling, stable hydrate structures, cell parameters, and surface energies, as well as the self-assembly and dynamics of surfactants on its surface. These computational methods provide quantitative agreement with experimental data and reveal key aspects of clay-water and clay-cation interactions, leading to a comprehensive understanding of the material's structure, dynamics, and energetics (Cygan, 2009).

The computational approach allows for a detailed exploration of montmorillonite properties. Quantum mechanical methods enable the precise computation of cell parameters, surface energies, and interface energies of clay minerals, which show quantitative agreement with experimental results. The interactions between clay layers, water (hydration/dehydration dynamics), and cations within the interlayer spaces can be accurately simulated and explored. The phenomenon of crystalline swelling, which is the expansion of the clay layers due to water uptake, is now well-understood and thermodynamically stable layer hydrates have been identified. The self-assembly and dynamics of surfactants on the surfaces of clay minerals can be accurately modelled and studied, providing insights into surface chemistry.

Despite these advances, several limitations remain in previous computational studies. Earlier works on montmorillonite using the DFT method did not optimize the structure first and only used one type of

cation and used a different DFT method by not using van der Waals (dispersion) correction (DFT-D3) as in this study (Lavikainen et al., 2015; Lavikainen et al., 2016; Wungu et al., 2011; Wungu et al., 2016). Previous studies that have done research on one unit cell and one type of layer charge for various types of cations Berghout, et al., 2010). This provides an opportunity for this study to find out in more depth and detail related to the most stable montmorillonite structure. The clay computation that has been carried out is expected to provide a basic knowledge base related to the material structure and prediction of the properties possessed by saturated montmorillonite in different layer charges.

The main focus of this study is the optimization of saturated montmorillonite with different interlayer cation (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) using DFT-D3 method to obtain the most stable structure through computational calculations and its properties. Optimization was carried out by varying the octahedral structure ($tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$), the amount and position of Mg^{2+} to substitute Al^{3+} in the octahedral structure, then also varying the placement of interlayer cation in the interlayer layer to compensate for the negative charge on the surface of the structure caused by the substitution.

The results of this research are expected to contribute to a fundamental understanding of structure-property relationship in homoionic saturated montmorillonite and to provide a theoretical basis for predicting its behaviour under various physicochemical conditions.

3.2 Methods

3.2.1 Model Structure

The structural model used is as described in section 2.1.1.

3.2.2 Optimization of Homoionic Saturated Montmorillonite Structures

The optimization of homoionic saturated montmorillonite structure with different type of cation interlayer and different octahedral structure in different d001 interval structural is described in section 2.1.2.

3.2.3 Computational Chemistry Method

The parameters used in the Computational Chemistry Method, the software used, and the parameters of the atoms involved in homoionic saturated montmorillonite structures are described in section 2.1.5.

3.3 Results and Discussion

The six basic structures obtained from the modified structure of Tsipurski and Drits (Tsipursky and Drits, 1984) both Na^+ - and K^+ -saturated montmorillonite have similarities in the position of sodium and potassium which occupy a position in the middle of the interlayer. The difference between the three structural forms of $tv \text{Mg}_{cis}$, $cv \text{Mg}_{cis}$ and $cv \text{Mg}_{trans}$ is the position of magnesium which substitutes aluminum in the octahedral layer. The orientation direction of the OH group in the $tv \text{Mg}_{cis}$ structure is parallel to the a-axis, while in the $cv \text{Mg}_{cis}$ and $cv \text{Mg}_{trans}$ structures the orientation direction of the OH group is not parallel to the a-axis.

3.3.1 Cation position, distance Mg-Mg in octahedral layer and stability of simples saturated montmorillonite structure

The optimization of the $1 \times 1 \times 1$ and $2 \times 1 \times 1$ model in the c range used refers to previous research, $c = 9.6 - 10.7 \text{ \AA}$ (OW: $9.6-10.7 \text{ \AA}$) (Emmerich, 2018). In the literature, PW91 functional is used while in this study PBE functional with van der Waals disperse force correction (DFT-D3) is used. In this study, the c range used are $c = 9.10 - 9.90 \text{ \AA}$ for Na^+ -saturated montmorillonite, $c = 9.30 - 10.50 \text{ \AA}$ for K^+ -saturated montmorillonite and $c = 9.30 - 9.80 \text{ \AA}$ for Ca^{2+} - and Mg^{2+} -saturated montmorillonite. There is a shift in the range of c distances used from the previous method to the method used in this research because of the difference in methods between PW91 and PBE DFT-D3.

The c range selected in this study takes into account the similarity of the final structural shape after the calculations are completed and the structure is not damaged. In the $c < 9.10 \text{ \AA}$ region for the Na^+ -saturated montmorillonite structure and the $c < 9.30 \text{ \AA}$ region for the K^+ -, Ca^{2+} - and Mg^{2+} -saturated montmorillonite structure, structural changes are characterized by shifting the position of oxygen atoms in the tetrahedral so that the orientation direction of the tetrahedron shape changes, this structural change makes the data obtained from calculations unusable compared to data in a set of optimization c ranges.

Figure 3.1 shows a graph of the c-spacing function against Total Energy for each saturated montmorillonite. It can be seen that all the most stable structures of Na^+ , Ca^{2+} and Mg^{2+} -saturated montmorillonite have a value of $c = 9.65 \text{ \AA}$. Except for K^+ -saturated montmorillonite, which has differences $tv \text{Mg}_{cis}$, $cv \text{Mg}_{cis}$ and $cv \text{Mg}_{trans}$ are 10.10 , 10.10 and $10.25 \text{ \AA}$, respectively. The size of K^+ ($2.35 \text{ \AA}$) requires a larger interlayer space compared to the other three cations, which are $< 1.97 \text{ \AA}$. Larger cations not only require more space but also cause repulsion between atoms and atoms in the 2:1 layer, resulting in interlayer spacing expansion. where larger cations not only occupy more interlayer space but also introduce repulsive forces with neighbouring atoms due to their strong electronic interactions, leading to weakened interlayer bonding and the formation of interlayer spacing expansion. The interlayer expansion is affected by size of the intercalated alkali metal ions (Xu, et al., 2017).

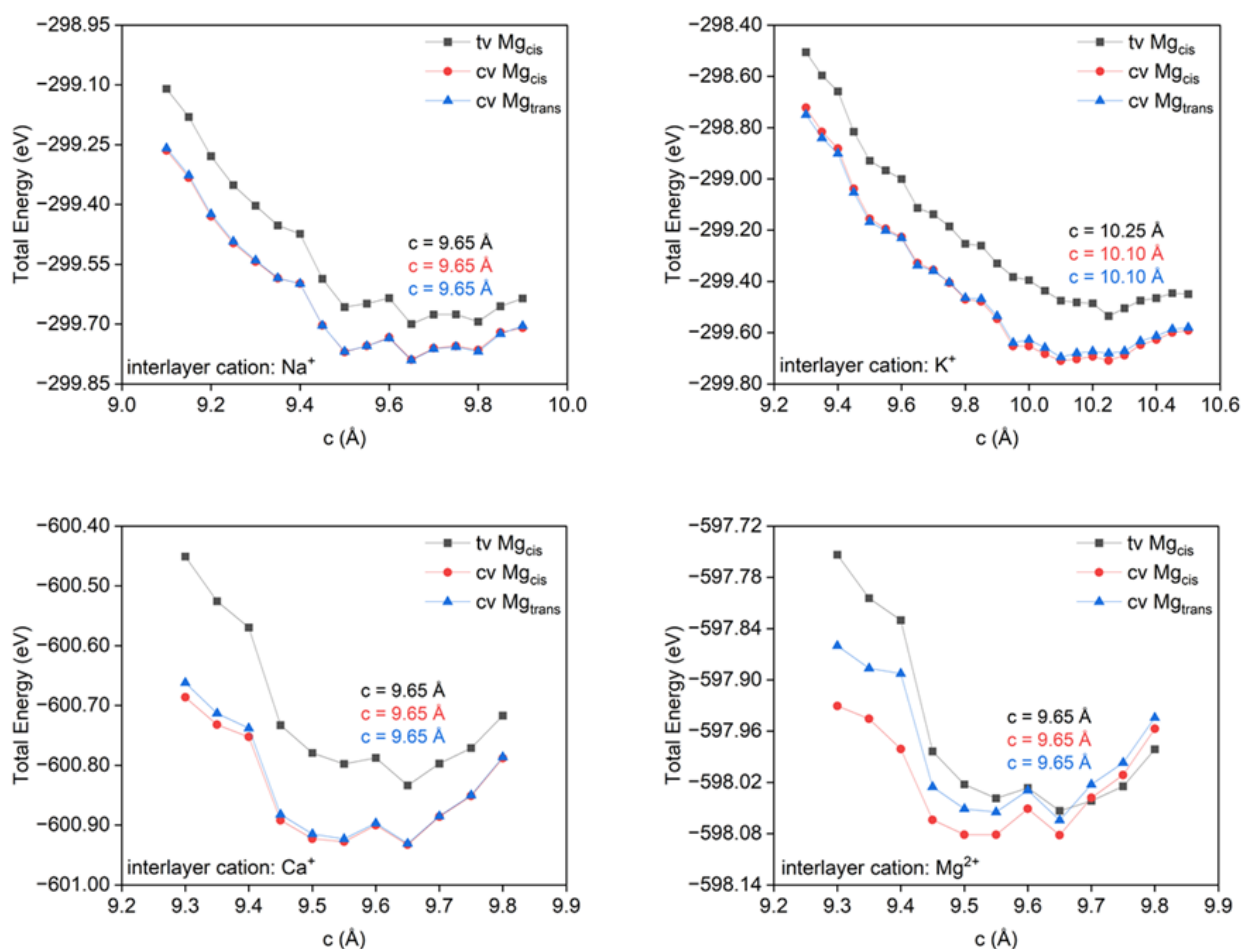


Figure 3.1: Total Energy (eV) as function of c-spacing

The position of cations in the interlayer tends to be close to the Mg^{2+} substitution position in the octahedral layer and occupies the space directly above the tetrahedral hole. The positions of Na^+ and K^+ cations are almost identical for all structures, as are those of Ca^{2+} cations, which occupy positions almost identical to those of interlayer Mg^{2+} cations (Figure 3.2, 3.3, 3.4 and 3.5). The substitution of Al^{3+} with Mg^{2+} in the octahedral layer causes an excess of negative charge around the substitution area, causing the cation position to approach the electron-rich area to balance the charge in the entire montmorillonite structure. Isomorphic substitutions in montmorillonite sheets such as Mg^{2+} substituting for Al^{3+} in octahedral layers and Al^{3+} substituting for Si^{4+} in tetrahedral layers result in negatively charged layers. The negatively charged layers are compensated by exchangeable cations in the interlayer region (Velde and Meunier 2008; Zhu et al., 2016).

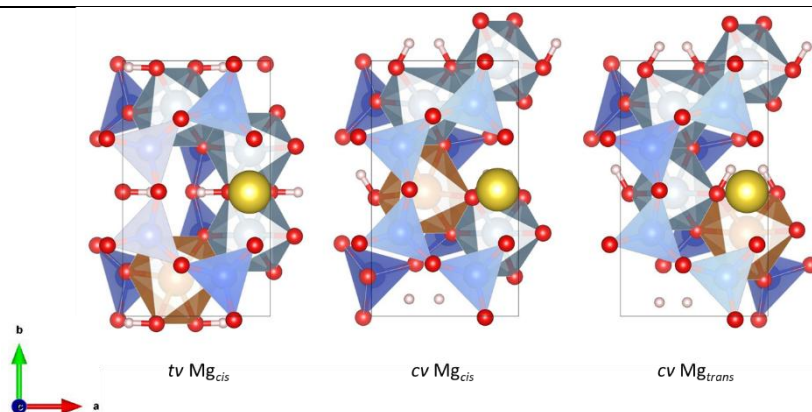


Figure 3.2: Optimized Structures of 1x1x1 models of Na⁺-saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium

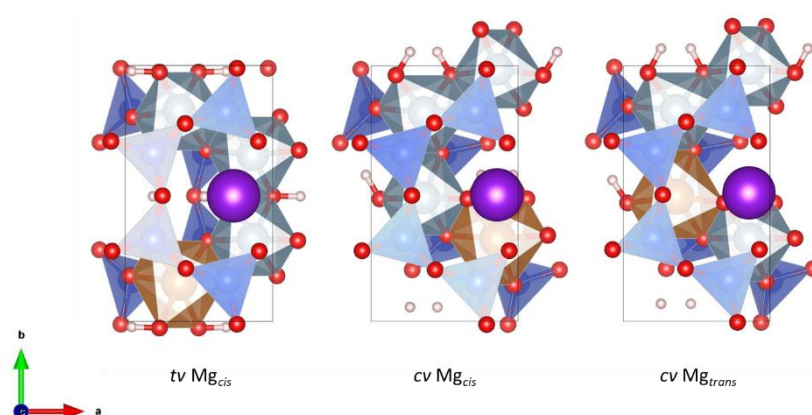


Figure 3.3: Optimized Structures of 1x1x1 models of K⁺-saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium

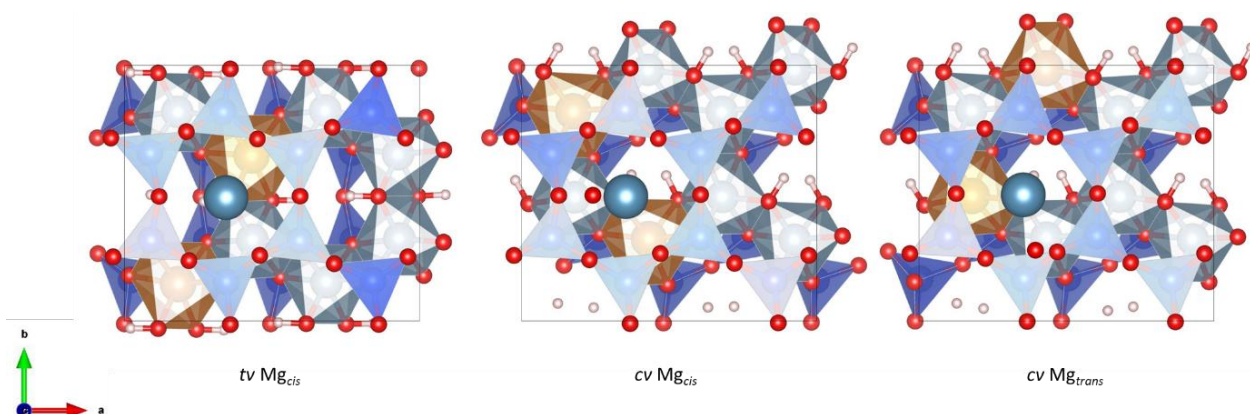


Figure 3.4: Optimized Structures of 2x1x1 models of Ca²⁺-saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium

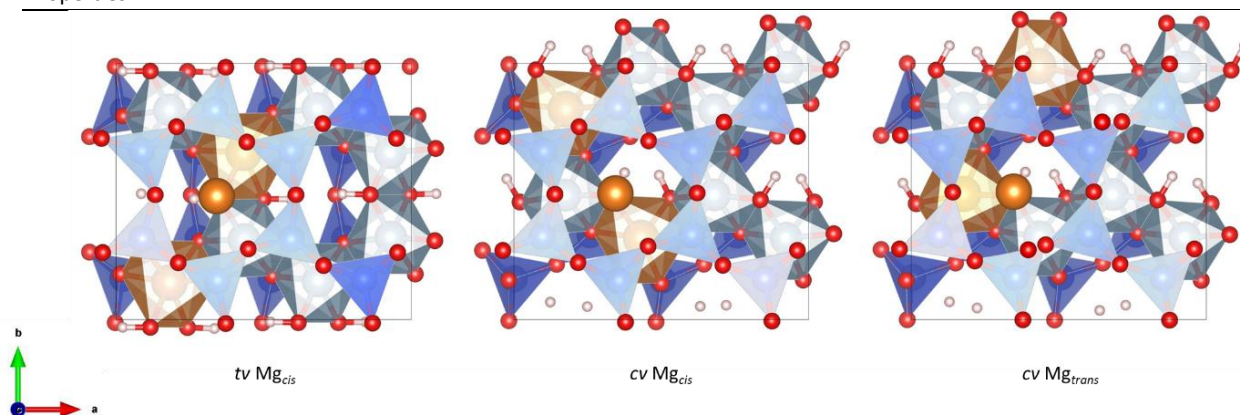


Figure 3.5: Optimized Structures of 2x1x1 models of Mg^{2+} -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium

Testing of each possible supercell model with different layer charges aims to determine the effect of repetition of each unit cell on the a-axis and b-axis. Under natural conditions, each crystalline structure has a long-range order orientation in all directions in 3-dimensional coordinates. This test is to determine the effect of different number of repetitions of unit cells and different orientation directions of long-range order unit cells on the stability of the structure. The most stable structure is indicated by the lowest total energy for the same layer charge and the same number of unit cells. This test was performed on the simplest structure for each different layer charge in all $tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ Na^+ -, K^+ -, Ca^{2+} - and Mg^{2+} -saturated montmorillonite.

The calculation results for the Na^+ -saturated montmorillonite structure $tv \text{ Mg}_{cis}$ (Table S1) and $cv \text{ Mg}_{cis}$ (Table 2) show that the 4x1x1 supercell model has the highest stability compared to the 2x2x1 and 1x4x1 supercell models at layer charges of 0.125 and 0.375. The 2x1x1 supercell model is more stable than the 1x2x1 model at layer charges of 0.250 and 0.500. However, for the K^+ -saturated montmorillonite structure (Table S3), the 4x1x1 supercell model has the highest stability compared to other structures at layer charges of 0.125 and 0.375. Unlike Na^+ -saturated montmorillonite, K^+ -saturated montmorillonite structures are most stable at layer charges of 0.250, 0.375, and 0.500, each with the same structural orientation, respectively 2x1x1, 2x2x1, and 2x1x1; The most stable structure in $tv \text{ Mg}_{cis}$ with a layer charge of 0.125 is 4x1x1, while in the $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ structures, it is 2x2x1. In divalent cations, all structures in each layer with different charges have the same orientation for all $tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ Ca^{2+} - and Mg^{2+} -saturated montmorillonite, namely, for charge layers 0.125, 0.250, 0.375 and 0.500, they are 4x2x1, 4x1x1, 4x2x1, and 2x2x1, respectively.

The stability of a montmorillonite crystalline structure depends on the distance between magnesium (Mg) atoms in its octahedral layers. Specifically, a larger distance between Mg atoms within these octahedral layers leads to a more stable structure because it minimizes repulsive forces between the Mg atoms, allowing them to exist in a more energetically favourable configuration (Figures S1-S6). The calculation results using the DFT-D3 method also show that the entire structure of Na^+ -saturated montmorillonite is more stable than K^+ -saturated montmorillonite at the same layer charge and the same vacant type; and for divalent cation, Ca^{2+} -saturated montmorillonite is more stable than Mg^{2+} -saturated montmorillonite.

3.3.2 Basal Space of Saturated Montmorillonite

The convergence of the atomic configuration of each type of structure ($tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$) with different layer charge (layer charge: 0.125, 0.250, 0.375 and 0.500) was tested by performing a series of calculations with different layer thickness (c). The testing range for the entire Na^+ -saturated montmorillonite structure was $c = 9.10 - 9.90 \text{ \AA}$, K^+ -saturated montmorillonite structure was $c = 9.30 - 10.40 \text{ \AA}$ and Ca^{2+} - and Mg^{2+} -saturated montmorillonite structure was $c = 9.10 - 10.0 \text{ \AA}$. Both ranges were obtained from the results of a series of previous tests using the simplest structure in the previous section. Areas with distances lower than those mentioned above undergo structural changes characterised by a shift in the position of oxygen atoms in the tetrahedron, thereby altering the shape of the tetrahedron. In other words, the structure becomes unbalanced (damaged), rendering the calculated data unusable or incomparable within the intended optimisation range. Figures 3.6, 3.7, 3.8, and 3.9 are graphs of the d_{001} function against Total Energy (eV) from the convergence calculation results of the atomic configuration of each type of structure ($tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$) with different layer charges (layer charges: 0.125, 0.250, 0.375, and 0.500) at different layer thicknesses (c). A simpler and more comprehensive summary of the results is presented in Table S13.

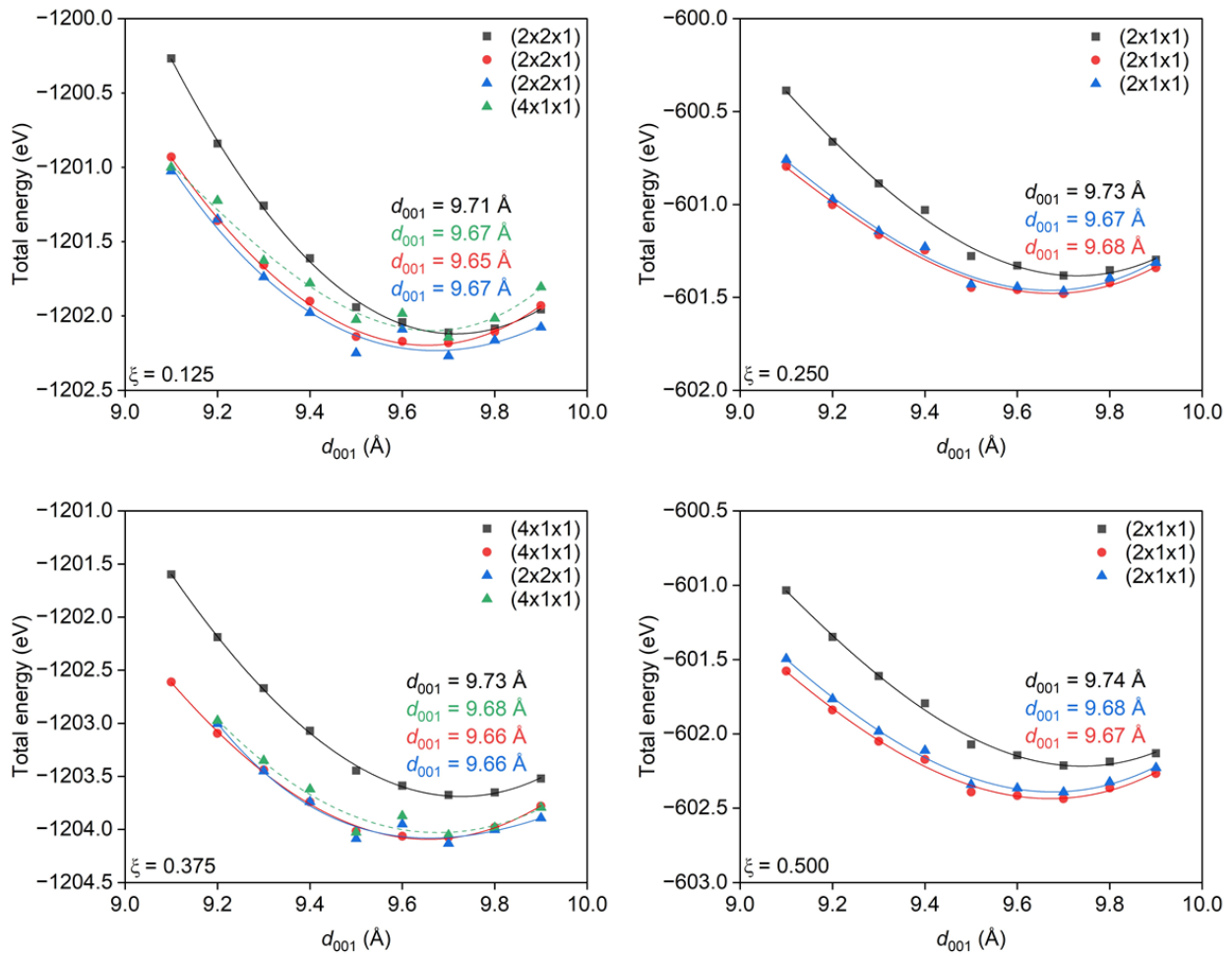


Figure 3.6: Basal space of Na^+ -saturated montmorillonite (square: $tv \text{ Mg}_{cis}$, circle: $cv \text{ Mg}_{cis}$ and triangle: $cv \text{ Mg}_{trans}$), supercell size in parenthesis

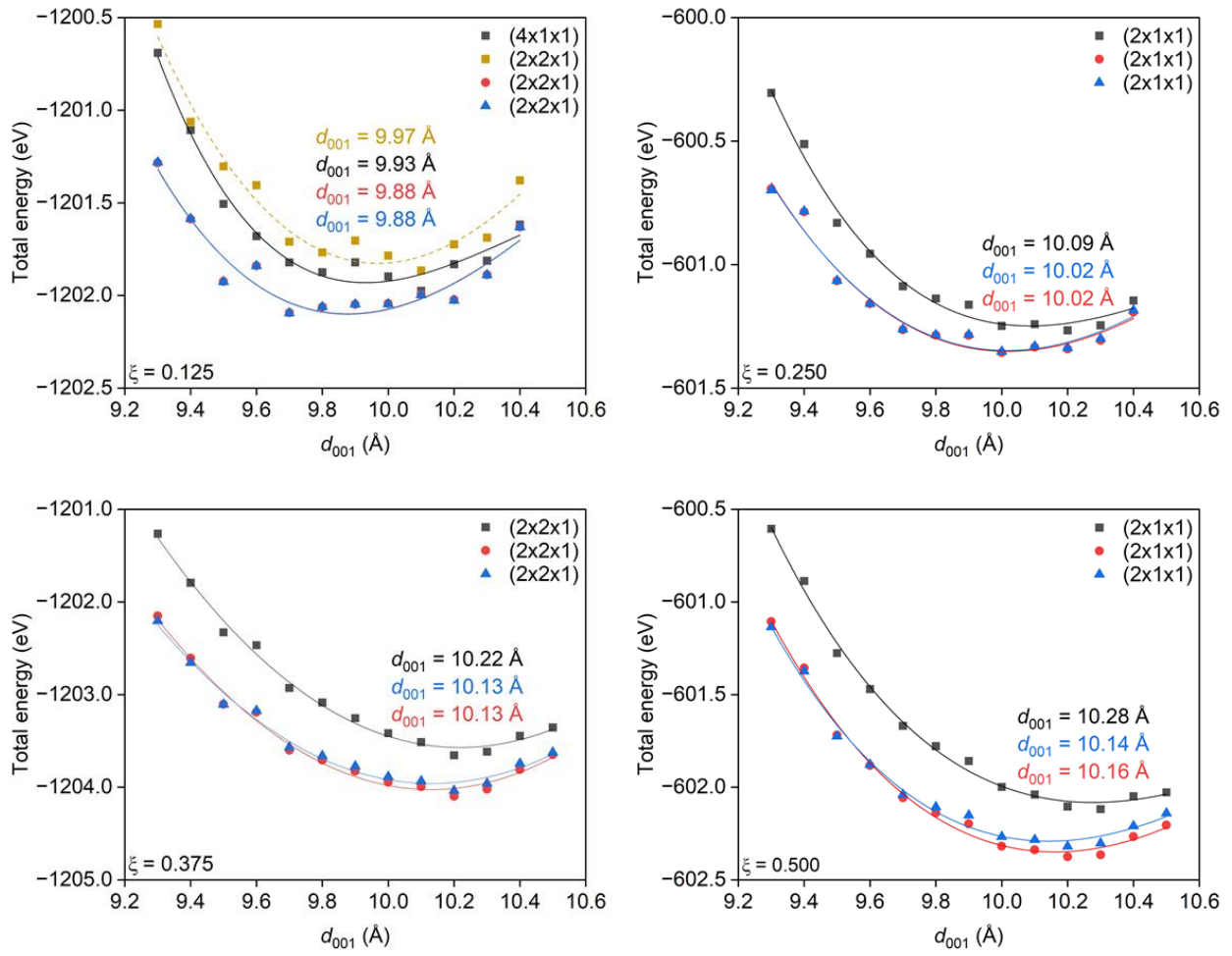


Figure 3.7: Basal space of K⁺-saturated montmorillonite (square: $tv \text{ Mg}_{cis}$, circle: $cv \text{ Mg}_{cis}$ and triangle: $cv \text{ Mg}_{trans}$), supercell size in parenthesis

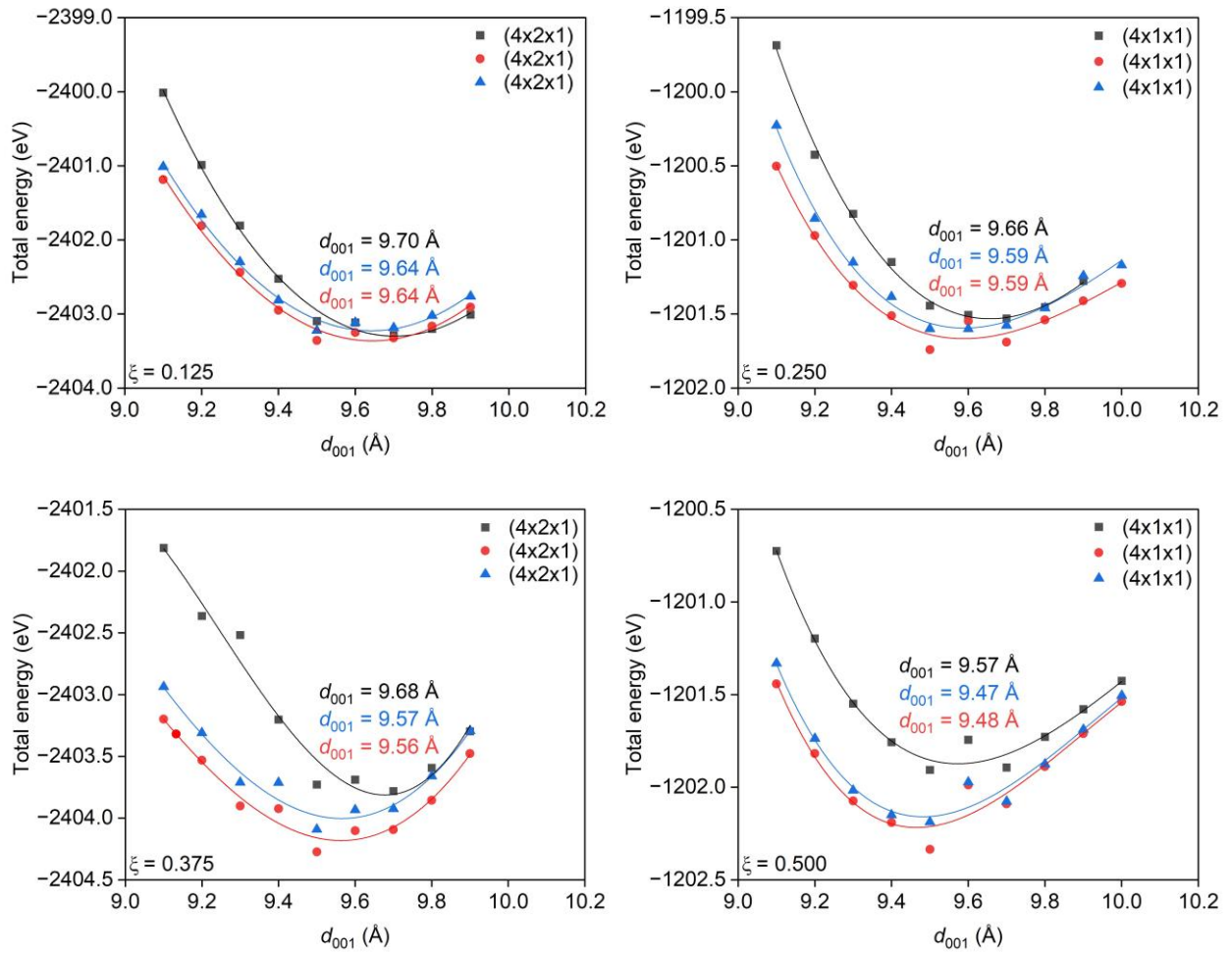


Figure 3.8: Basal space of Ca^{2+} -saturated montmorillonite (square: $\text{tv Mg}_{\text{cis}}$, circle: $\text{cv Mg}_{\text{cis}}$ and triangle: $\text{cv Mg}_{\text{trans}}$), supercell size in parenthesis

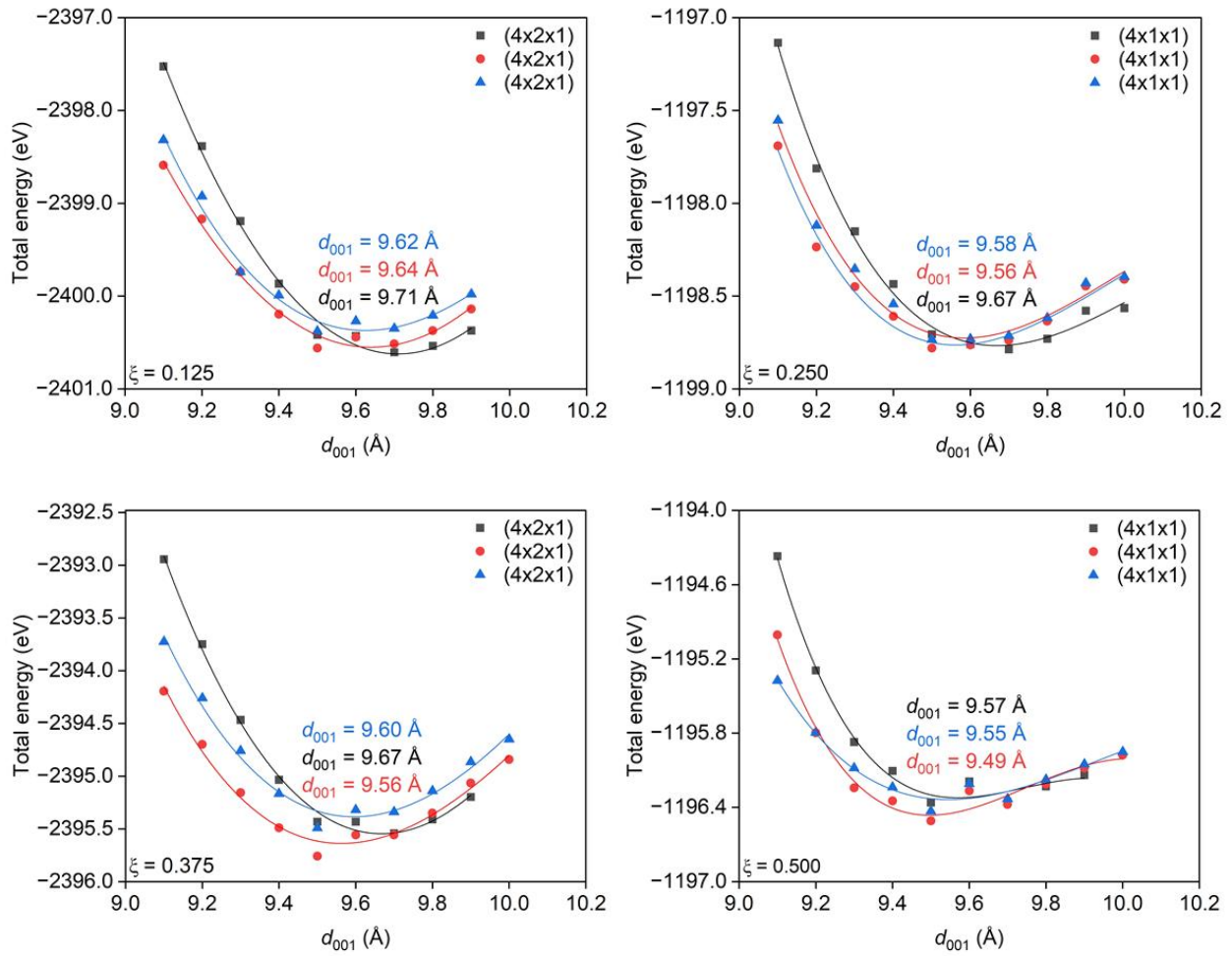


Figure 3.9: Basal space of Mg^{2+} -saturated montmorillonite (square: $tv \text{Mg}_{cis}$, circle: $cv \text{Mg}_{cis}$ and triangle: $cv \text{Mg}_{trans}$), supercell size in parenthesis

From results it can also be seen that the optimum c of Na^+ -saturated montmorillonite is smaller than that of K^+ -saturated montmorillonite for all three $tv \text{Mg}_{cis}$ structures, $cv \text{Mg}_{cis}$ and $cv \text{Mg}_{trans}$. This is because the size of the diameter of the potassium atom is larger than the diameter of the sodium atom. The larger atomic diameter size results in potassium atoms requiring a larger space compared to sodium atoms in the interlayer. In addition, the repulsion between the outermost electrons of the potassium atoms and the oxygen atoms in the tetrahedral layer is greater than the repulsion between the outermost electrons of the sodium atoms and the oxygen atoms in the tetrahedral layer in the same layer structure. This also occurs in the comparison between Ca^{2+} - and Mg^{2+} -saturated montmorillonite, where the smaller Mg^{2+} size causes the optimum c distance for Mg^{2+} -saturated montmorillonite to be smaller than that for Ca^{2+} -saturated montmorillonite.

For all structure, indicated that d_{001} for $tv \text{Mg}_{cis}$ is higher than $cv \text{Mg}_{cis}$ and $cv \text{Mg}_{trans}$ at each layer charge. This indicates that the repulsion of sodium atoms with tetrahedral layers is higher in the $tv \text{Mg}_{cis}$ structure compared to the $cv \text{Mg}_{cis}$ and $cv \text{Mg}_{trans}$ structures. And also, Total Energy (eV) $cv \text{Mg}_{cis}$ and/or $cv \text{Mg}_{trans}$ lower than $tv \text{Mg}_{cis}$, it is indicated that cv more stable than tv in all structure of saturated montmorillonite.

In monovalent cations, there is an increase in d_{001} as the layer charge increases. Meanwhile, in divalent cations, there is a decrease in d_{001} as the layer charge increases. An increase in layer charge strengthens the attraction to the negative charges on the layers of an ion-exchange material. In the presence of monovalent cations, this increased electrostatic attraction can lead to an expanded interlayer spacing as the cations become more strongly hydrated and occupy more space to balance the stronger charge deficit. Divalent cations have a stronger electrostatic interaction than monovalent cations due to their higher charge. When the layer charge increases, divalent cations can be more tightly bound between the layers, leading to a more compressed structure and a decrease in the d_{001} .

3.3.3 Basal Space and Specific Density Variations

In an orthogonal crystal structure, the basal spacing (d_{001}) is equivalent to the lattice constant c_0 . Montmorillonites with alkali interlayer cations show an increased basal spacing with higher layer charge, whereas those with earth alkali cations experience a decrease. Generally, the *tv* structures of montmorillonite exhibit larger basal spacings than *cv* structures.

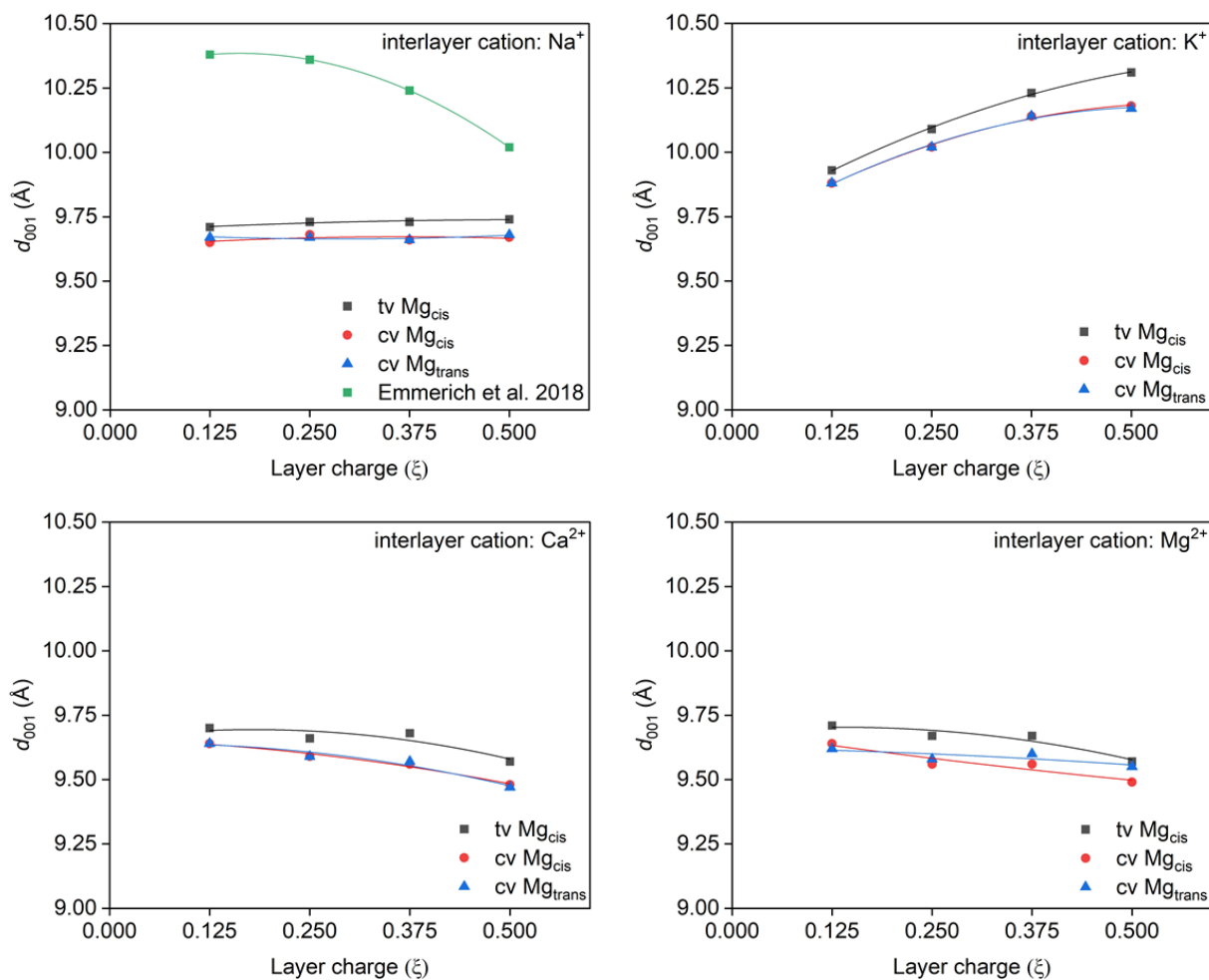


Figure 3.10: Basal spacing of saturated montmorillonite as function of layer charge

While calculations accounting for dispersion forces showed minimal expansion in the basal space of Na^+ -saturated montmorillonites with increasing layer charge, Emmerich et al. (2018) found a significant increase in basal spacing and even a decrease in some cases when using the PW91 functional without dispersion correction, according to their study (Figure 3.10; top-left).

Mg^{2+} -saturated montmorillonites have the smallest basal spacing (9.47–9.74 Å), similar to Ca^{2+} and Na^+ forms, while K^+ -saturated montmorillonites have significantly larger spacings (9.88–10.31 Å), a trend consistent with prior research on similar clays but with greater variability in reported spacing values for the former cations (Figure 3.10). These trends agree with previous studies (e.g., Voora et al., 2011) who reported a similar trend of basal spacing for homoionic trans-vacant montmorillonites of layer charge 0.5, though with a large variation in the reported values (9.12 - 10.44 Å) for Na^+ , Ca^{2+} - and Mg^{2+} -saturated montmorillonites, and 9.73 - 10.66 Å for K^+ -saturated montmorillonite. While dispersion corrections in DFT calculations generally lower d_{001} values, they did not lead to a consistent improvement or pattern in the optimization results concerning all lattice parameters or just the c-axis and d_{001} parameters, as also noted in other studies Voora et al. (2011) and Li et al. (2016). Experimental data for homoionic montmorillonites with varying layer charges reveals that the calculated basal spacing (d_{001}) is higher than expected because insufficient drying left residual water in the clay layers, even in samples that were supposed to be anhydrous. The larger calculated basal spacing (d_{001}) of K^+ -saturated montmorillonites compared to Na^+ , Ca^{2+} - and Mg^{2+} -saturated montmorillonites aligns with experimental findings, but MD simulations of anhydrous montmorillonites typically yield smaller d_{001} values than DFT studies, with Mg^{2+} -saturated montmorillonite showing an unusually large d_{001} (Skipper et al., 1991).

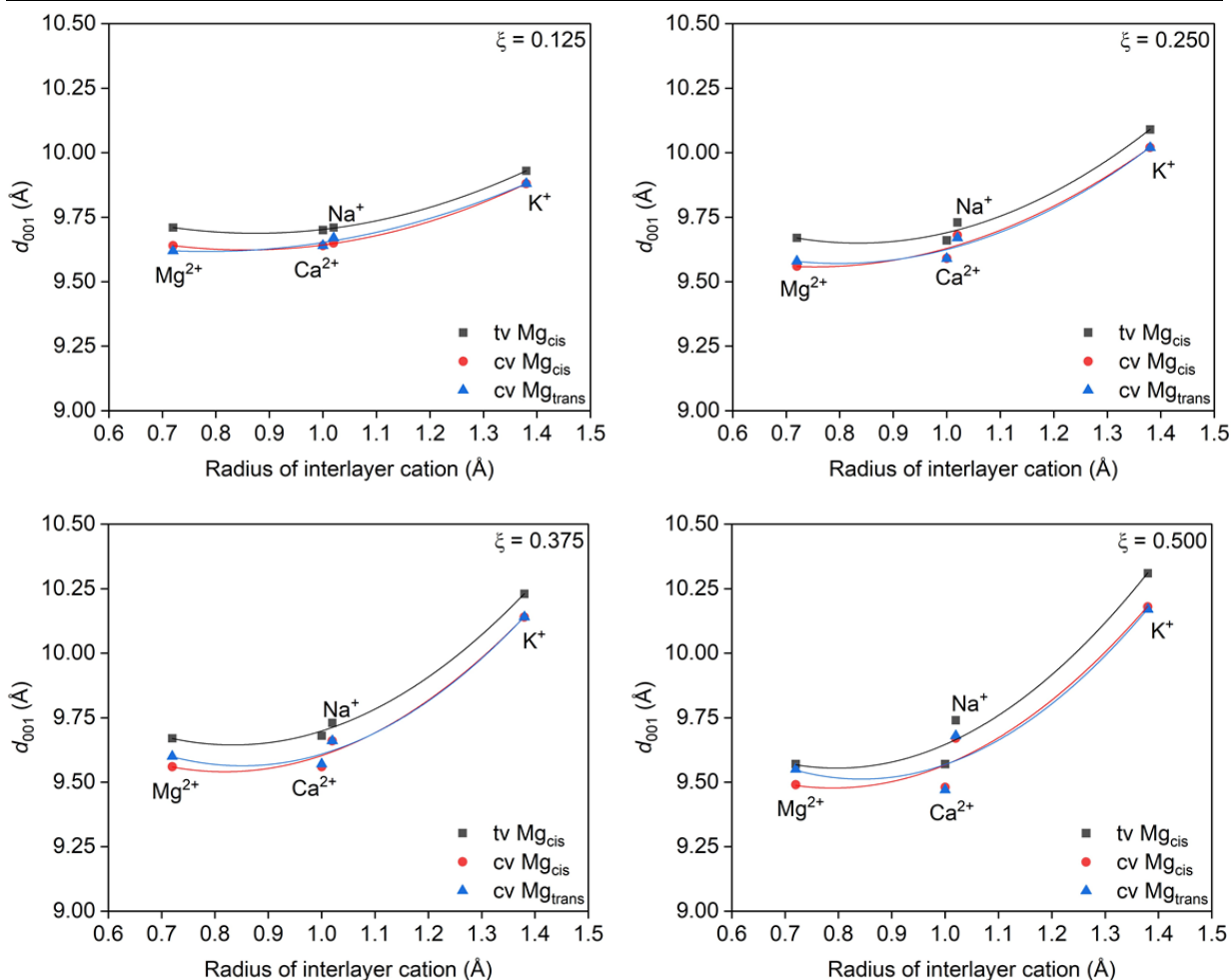


Figure 3.11: Basal spacing of saturated montmorillonite as function of radius of interlayer cation

Unit cell volume is the largest for K^+ -saturated montmorillonites, resulting in lower specific density (2.61–2.66 g/cm³), which decreases between layer charges of 0.125 to 0.375 and increases again at layer charge of 0.5. In contrast, Na^+ , Ca^{2+} , and Mg^{2+} -saturated montmorillonites show higher specific densities (2.66–2.78 g/cm³), which increase with increasing layer charge (Figure 3.12).

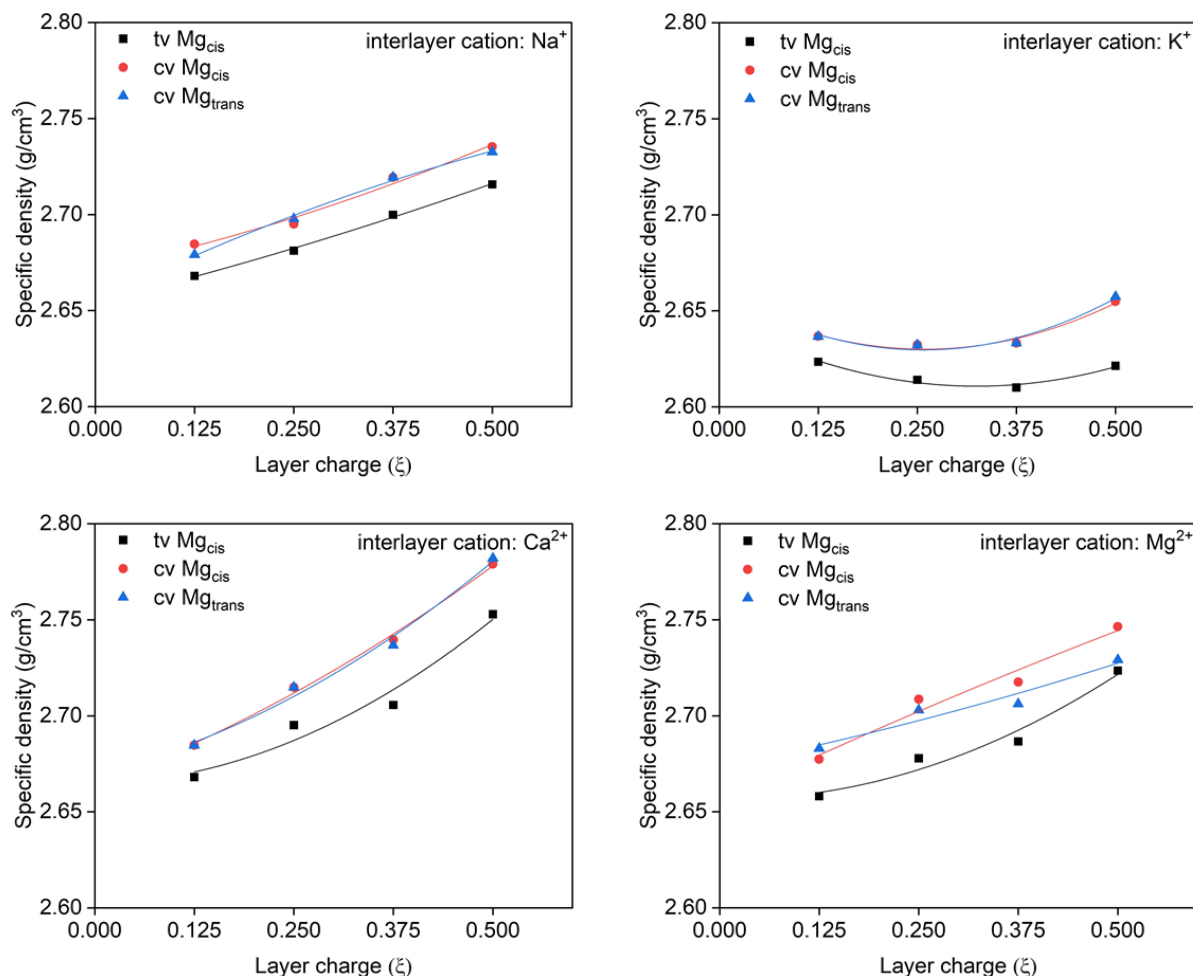


Figure 3.12: Specific density of saturated montmorillonite as function of layer charge

3.3.4 Layer Thickness, Position of Interlayer Cations and Interlayer Thickness

While d_{001} varies significantly with the type of interlayer cation and layer charge, the thickness of the 2:1 layer is rather constant across all structures. The average layer thickness is $6.79 \pm 0.04 \text{ \AA}$ (Figure 3.13, 3.15 and 3.17), except for the cv Mg_{cis} layers of the Mg^{2+} -saturated montmorillonites that layer thickness is at $6.87 \pm 0.01 \text{ \AA}$ (Figure 3.19).

In homoionic montmorillonites, the number of interlayer cations (interlayer cations) depends on layer charge, with one cation at 0.125 and 0.25, three at 0.375, and two at 0.5. These cations, rather than sitting in the middle of the interlayer, are typically found shifted toward the basal surface of the 2:1 layer. Mg^{2+} preferentially occupies the ditrigonal rings of the basal oxygens, and the distance to the basal surface follows the order $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Na}^+ < \text{K}^+$, with K^+ consistently residing near the interlayer centre.

The number of interlayer cations in the super cells varied with the layer charge: one for charges of 0.125 and 0.25; three for 0.375; and two for 0.5. In most optimized structures of homoionic montmorillonites, interlayer cations were not located half way up in the interlayer, but rather shifted toward the basal surface of the 2:1 layer. Among them, Mg^{2+} consistently occupied the ditrigonal rings

formed by the basal oxygen of the 2:1 layer, and the average distance to the surface of the 2:1 layer increased in the following order: $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Na}^+ < \text{K}^+$, with K^+ tend to reside near mid-interlayer region regardless of cation count.

A more complex behaviour of the Na^+ -saturated montmorillonites was observed. In the *tv* Mg_{cis} and *cv* Mg_{cis} structures with a layer charge of 0.375, one Na^+ was found at half height of the interlayer, while the two others were positioned approximately equidistant from both adjacent 2:1 layer. In the *cv* Mg_{trans} structure with a layer charge of 0.375, two Na^+ were found at half height of the interlayer, while the third resided closer to the 2:1 layer surface. At a layer charge of 0.5, and for all three structures, both Na^+ ions were found at the at half height of the interlayer. when using the Shannon (1976) ionic radii for a coordination number of 6, the effective diameters of Na^+ , Ca^{2+} , and Mg^{2+} are approximately 74%, 72%, and 52% of the diameter of K^+ , respectively.

When comparing the interlayer cations based on their effective ionic radius (coordination number = 6; Shannon, 1976), the diameter of Na^+ , Ca^{2+} and Mg^{2+} is 74, 72 and 52% of the that of K^+ . The interlayer opening is not determined by the size of the cation (Na^+ , Ca^{2+} , Mg^{2+} , K^+) because the percentages of opening are 88%, 85%, and 100% respectively, which does not correlate with their ionic radii. Instead, the changes in the d001 spacing are due to variations in the inter-layer space, driven by electrostatic and dispersion forces, rather than the specific interlayer cation's position or size. Na^+ -saturated montmorillonites exhibit a near-constant interlayer opening, K^+ -saturated ones show a strong increase, and Ca^{2+} - and Mg^{2+} -saturated montmorillonites experience a decrease with increasing layer charge.

Figures 3.14, 3.16, 3.18 and 3.20 are position mapping of cations in the interlayer. Contoured areas in the interlayer that can be occupied by cations. Based on these figures, cations in the interlayer can occupy different distances from the surface of the 2:1 layer depending on the negatively charged region resulting from the substitution of Al^{3+} by Mg^{2+} . The highly negatively charged region on the surface of the 2:1 layer causes cations to be attracted closer to the surface. the presence and distribution of negative charge from Mg^{2+} substitution for Al^{3+} in the 2:1 layer creates varying electrostatic forces that influence the distance of interlayer cations from the surface, attracting them closer to more highly charged regions. The role of the interlayer cations is to balance the negative charge of the layers (Bergaya and Lagaly, 2006) and cause the stacking of layers due to electrostatic interactions.

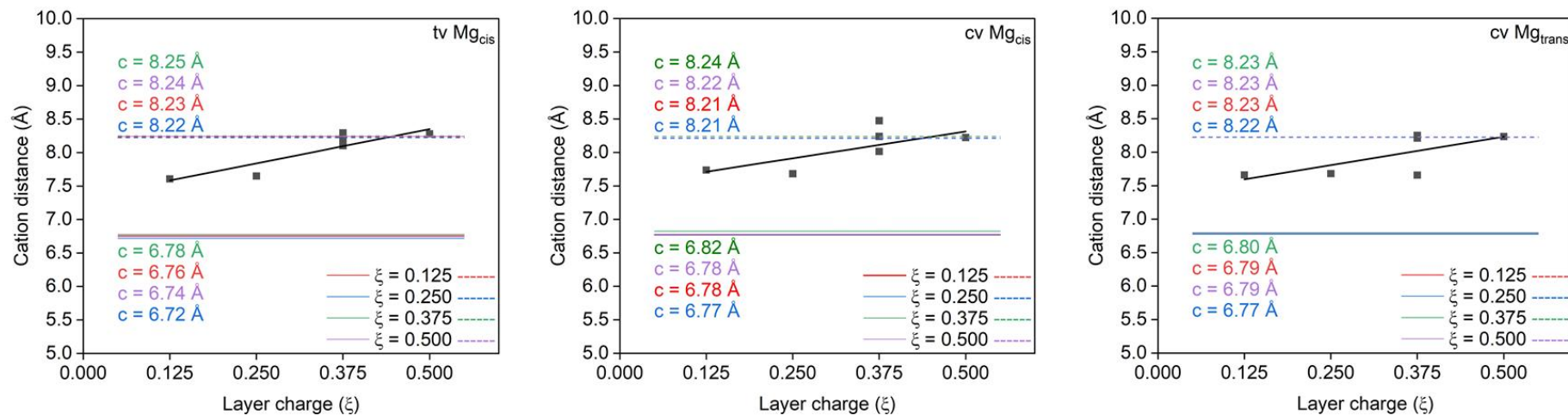


Figure 3.13: Position of interlayer cation of Na^+ -saturated montmorillonite in c-axis as function of layer charge (dashed line: the middle of the interlayer, line: layer thickness)

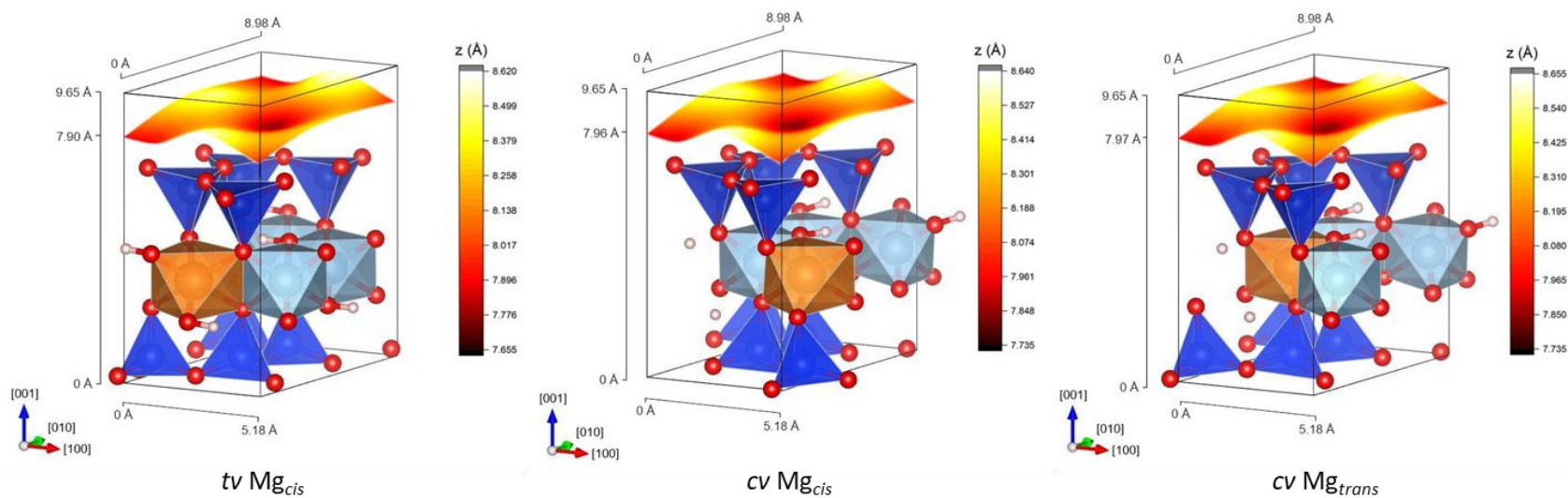


Figure 3.14: Position of interlayer cation Na^+ -saturated montmorillonite 1UC and $\xi = 0.500$

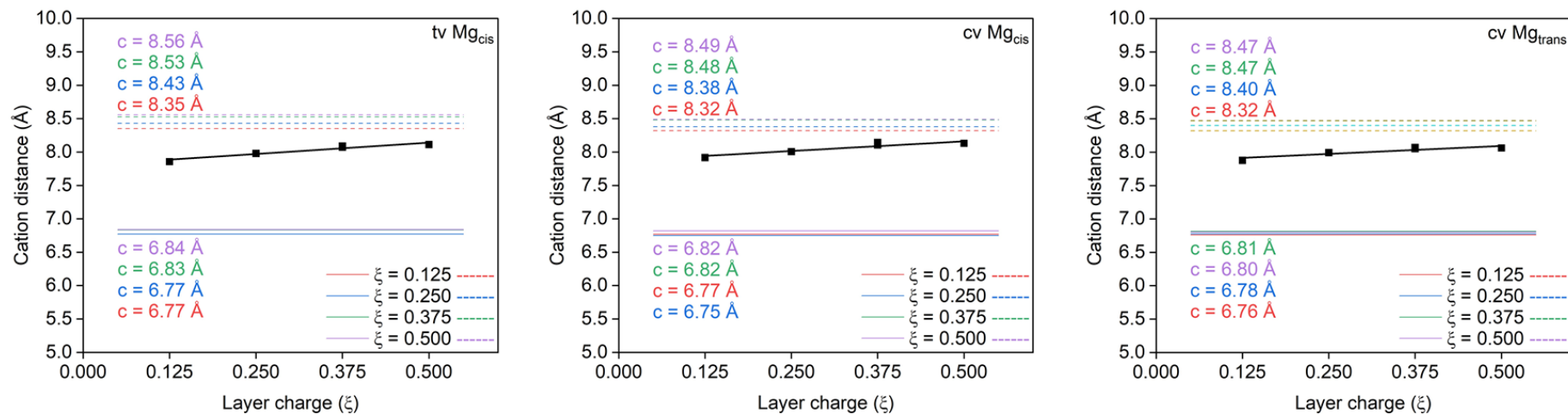


Figure 3.15: Position of interlayer cation of K^+ -saturated montmorillonite in c-axis as function of layer charge (dashed line: the middle of the interlayer, line: layer thickness)

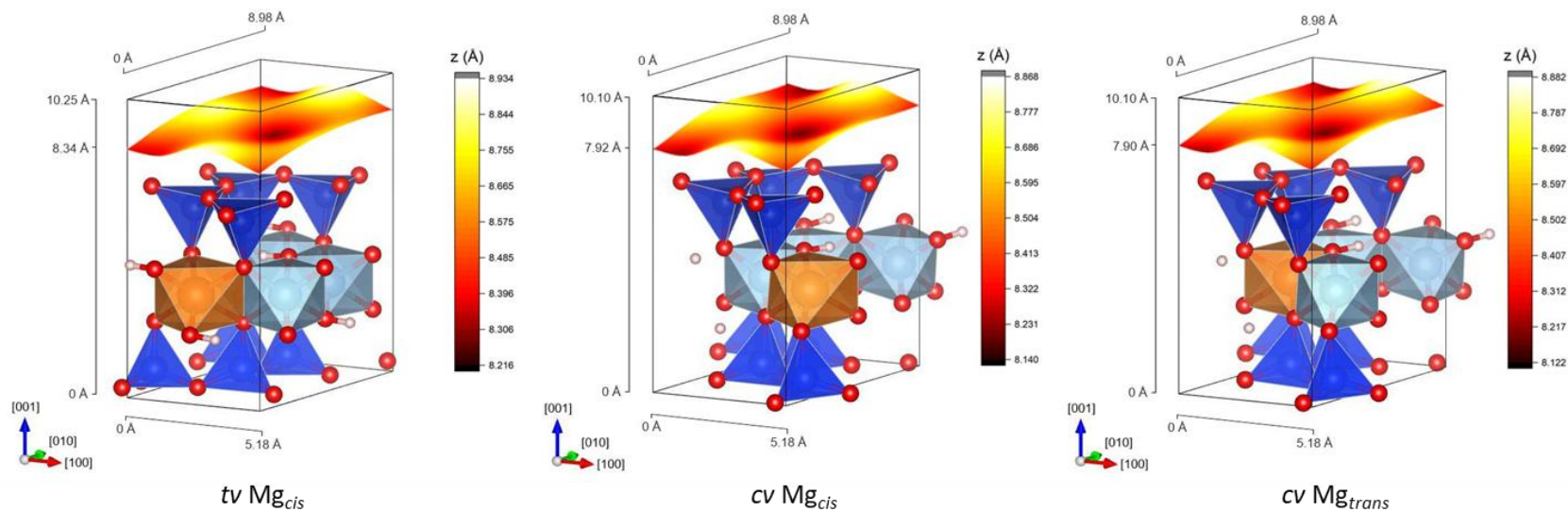


Figure 3.16: Position of interlayer cation K^+ -saturated montmorillonite 1UC and $\xi = 0.500$

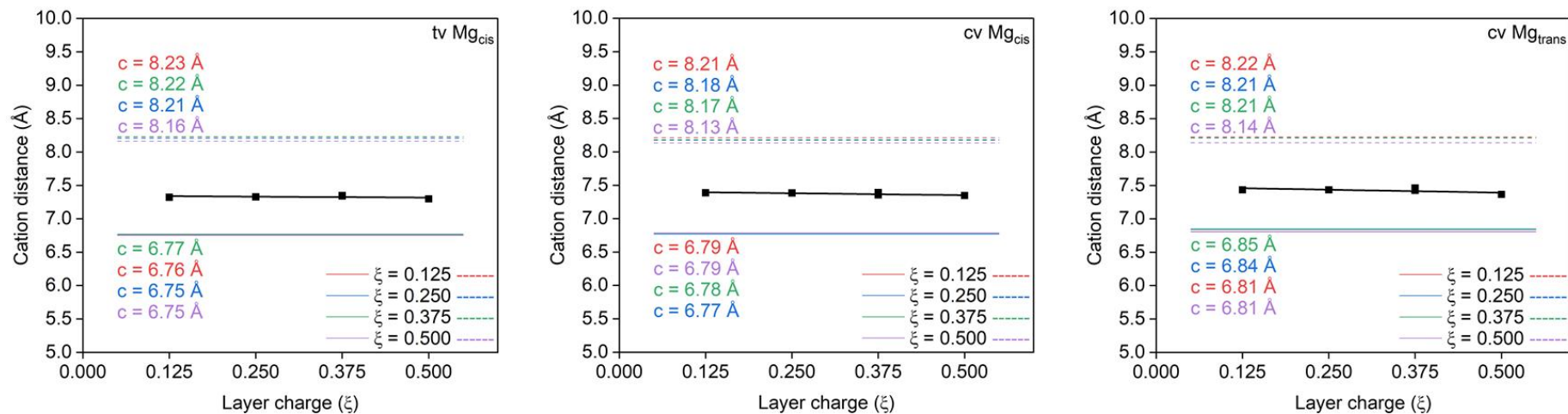


Figure 3.17: Position of interlayer cation of Ca^{2+} -saturated montmorillonite in c-axis as function of layer charge (dashed line: the middle of the interlayer, line: layer thickness)

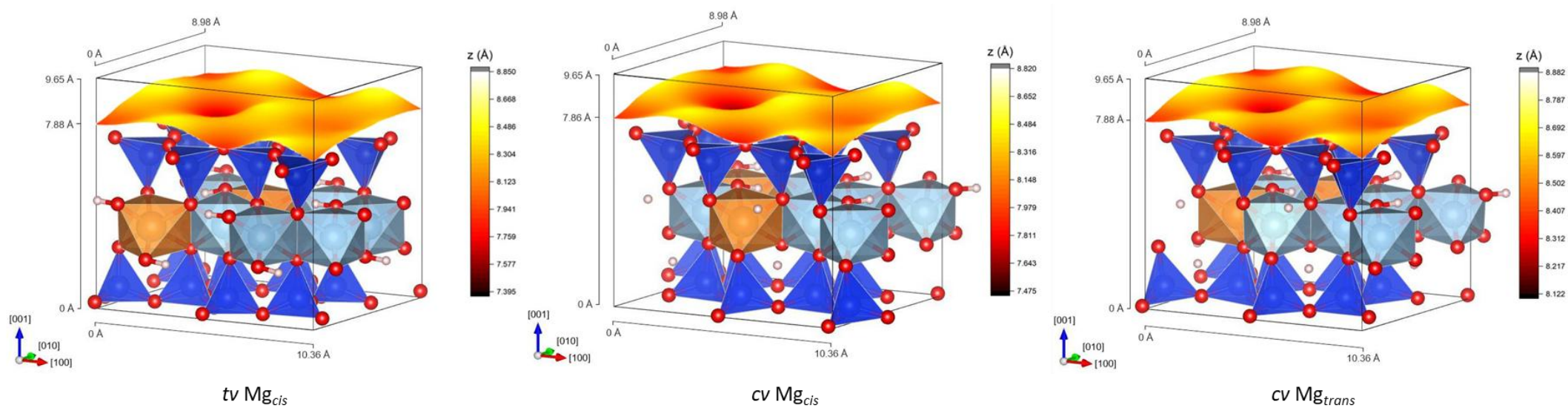


Figure 3.18: Position of interlayer cation Ca^{2+} -saturated montmorillonite 2UC and $\xi = 0.500$

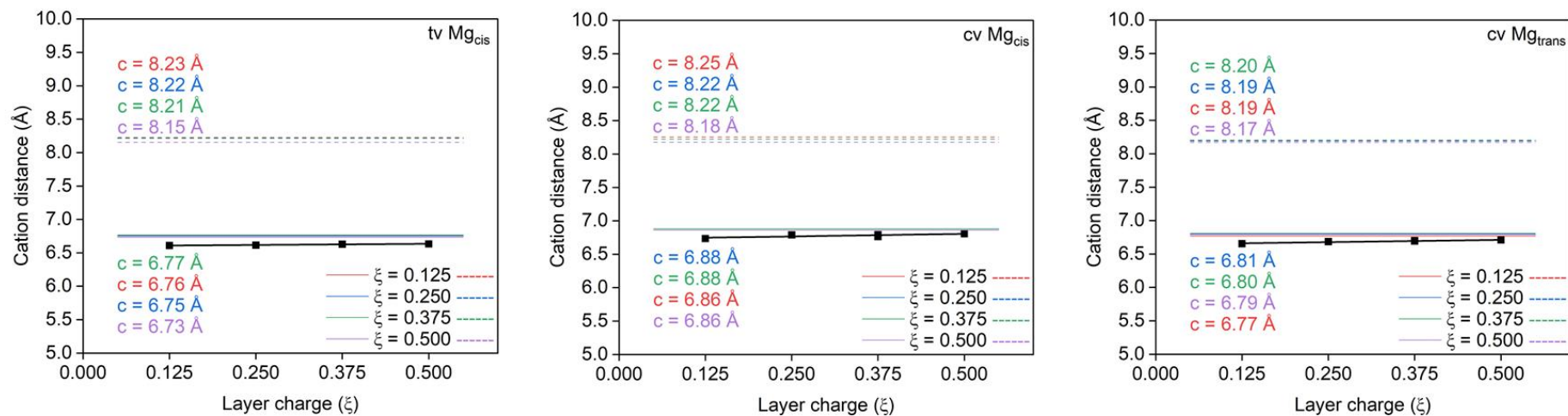


Figure 3.19: Position of interlayer cation of Mg^{2+} -saturated montmorillonite in c-axis as function of layer charge (dashed line: the middle of the interlayer, line: layer thickness)

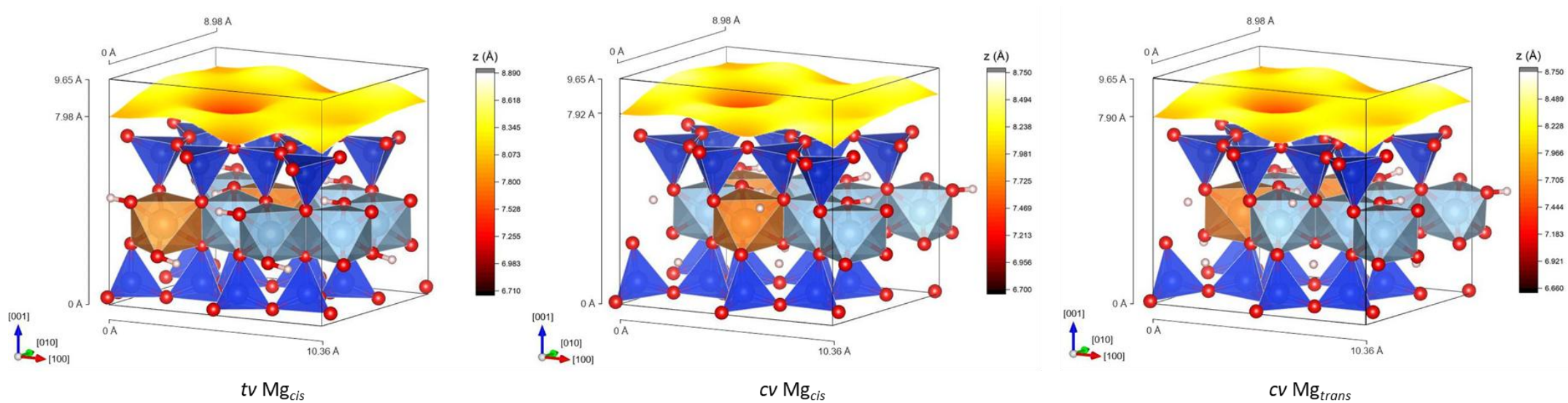


Figure 3.20: Position of interlayer cation Mg^{2+} -saturated montmorillonite 2UC and $\xi = 0.500$

3.3.5 OH Vectors Orientation

The orientation of hydroxyl (OH) groups is influenced by both the intrinsic layer charge (which determines the strength and number of interactions like Mg-OH-Al bonds) and the nature of the interlayer cations, as they interact with the hydroxyl groups and influence their alignment within the interlayer region. The orientation of an OH-vector within the ideal $C2/m$ symmetry of a clay's 2:1 layer is defined by a polar angle (ρ) relative to the (001) plane and an azimuthal angle (ψ) relative to the (010) mirror plane, with ψ always being less than 90° .

The OH vector is always oriented towards the octahedral vacancies and into the ditrigonal holes of the tetrahedral sheet, which means that the hydrogen is always located outside of the octahedral sheet (Figure 3.21 and 3.22). Therefore, the polar angle is always considered positive. The octahedral charge and position of interlayer cations in montmorillonite influence the spatial distribution (ρ) and orientation (ψ) of hydroxyl (OH) vectors by altering the effective charge density around the oxygen atoms, which affects H-bonding and the resulting structure of adsorbed water and counter-ions within the interlayer space. Higher octahedral charge from isomorphous substitution, or a cation's proximity to an OH-sharing Mg site, can lead to stronger electrostatic interactions, influencing the overall charge balance and hydrogen bonding network of the clay structure (Gates, et al., 2021).

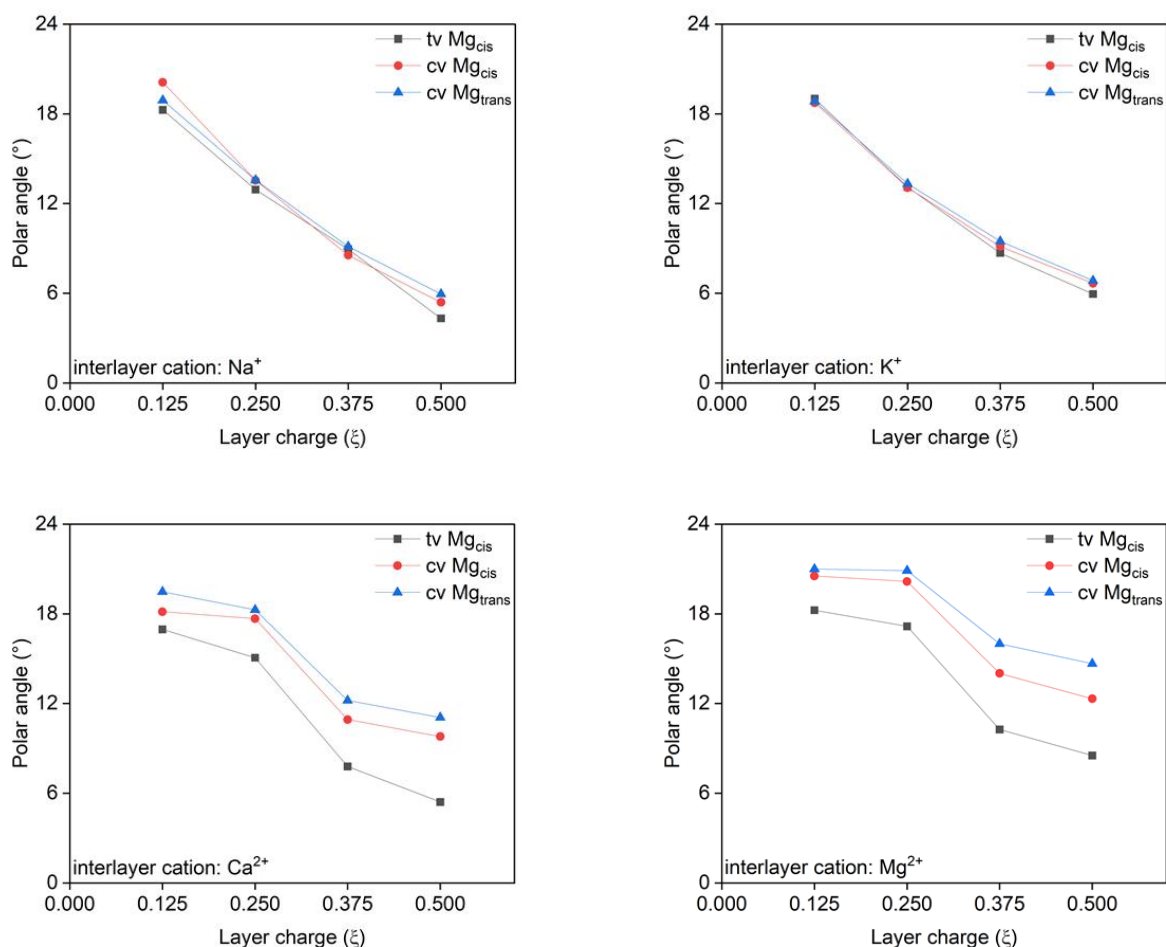


Figure 3.21: Averaged polar angle (ρ) of OH vector of homoionic saturated montmorillonites as function of layer charge

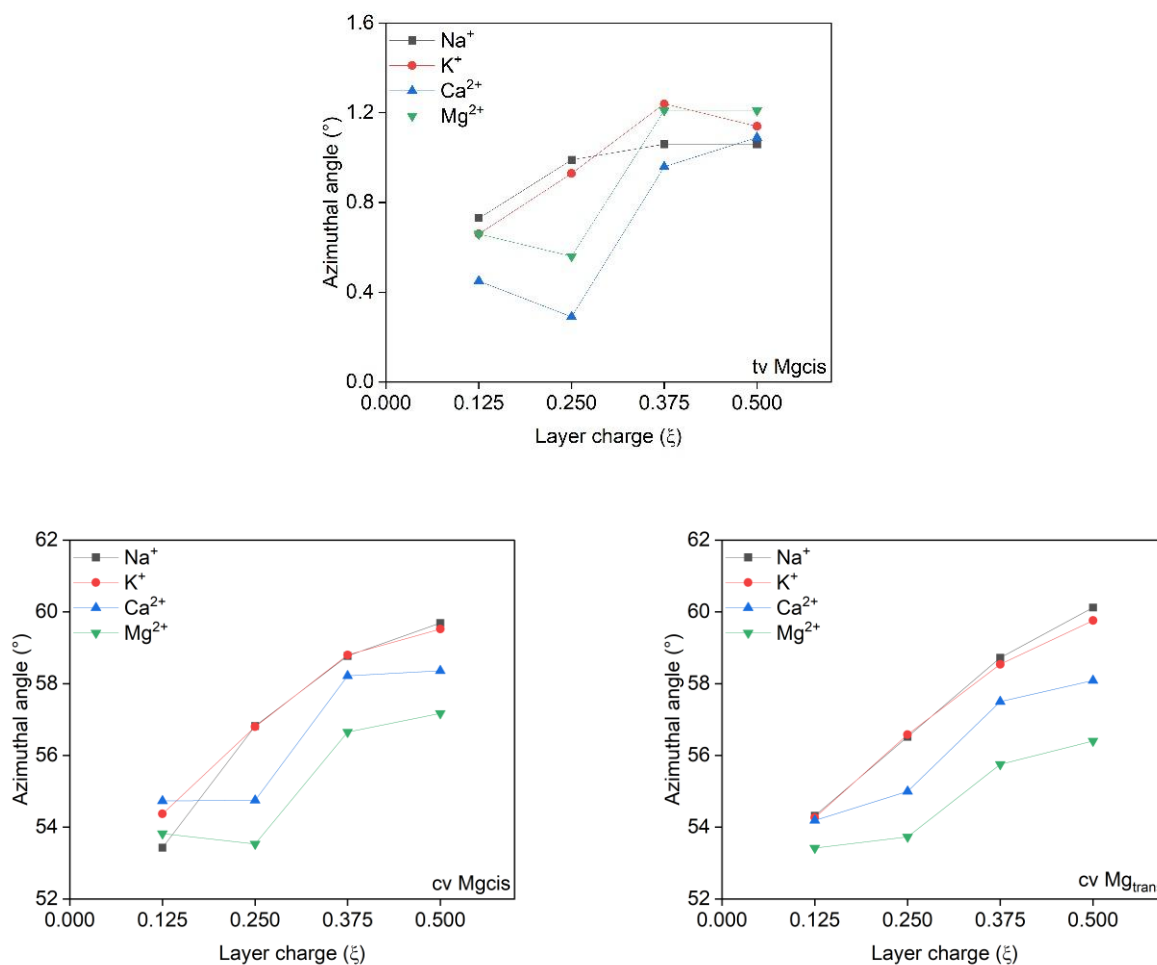


Figure 3.22: Averaged azimuthal angle (ψ) of hydrogen in octahedral hydroxyls of homoionic saturated montmorillonites as function of layer charge

3.3.6 Elastic Properties and Bulk Modulus of Anhydrous Homoionic Montmorillonites

The bulk modulus of anhydrous homoionic montmorillonites varies significantly based on the interlayer cation and layer charge. This indicates that different montmorillonite clays, with different cations and layer charges, will have varying resistance to volumetric compression, as represented by the bulk modulus (B or K), particularly under C33 conditions (parallel to the c_0 axis). The bulk modulus (B) of montmorillonite is higher for Na^+ -saturated samples (35–75 GPa) than for K^+ -saturated samples (20–30 GPa), and this modulus increases with the layer charge of the clay for both cations. This behavior is attributed to the different hydration characteristics of Na^+ and K^+ ions, with Na^+ ions being more outer-sphere and K^+ ions more inner-sphere, affecting interlayer spacing and overall material properties.

In contrast, B scattered around 40 GPa and 35 GPa for Ca^{2+} - and Mg^{2+} -saturated montmorillonites (Figure 8). These values are comparable in magnitude to the ones reported in Voora et al. (2011) at 42–59 GPa for a tv montmorillonite ($\xi = 0.5$) from DFT calculations, which also considered dispersive

forces. Voora et al. (2011) found that the B value (likely referring to the B parameter in montmorillonite) correlates with the type of interlayer cation, with Mg^{2+} -saturated montmorillonite showing the highest B value and K^+ -saturated montmorillonite the lowest, while Na^+ - and Ca^{2+} -saturated samples had similar, intermediate values. This indicates that different interlayer cations influence the properties of montmorillonite in distinct ways, affecting interactions and stability. Without consideration of dispersive forces in DFT calculations lower bulk moduli were obtained between 22 and 25 GPa for Mg^{2+} - and Ca^{2+} -saturated *tv* montmorillonite ($\xi = 0.5$) and 13 GPa for Na^+ -saturated *tv* montmorillonite ($\xi = 0.25$) (Berghout et al., 2010). The obtained range of bulk moduli perpendicular to the 2:1 layer lies in the range of young's moduli determined by nanoindentation of pyrophyllite ($E = 23.5$ GPa) and muscovite ($E = 5.4$ GPa) (Vaughan and Guggenheim, 1986; Zhang et al., 2010) assuming a Poisson's ratio of about 0.3 and is one order of magnitude higher than the bulk modulus of water (wikipedia, needs original ref: 2.08 GPa 10 °C, 0.1 MPa). In compacted bentonites the isotropic Young's modulus is about two orders of magnitude lower at about 0.15 GPa.

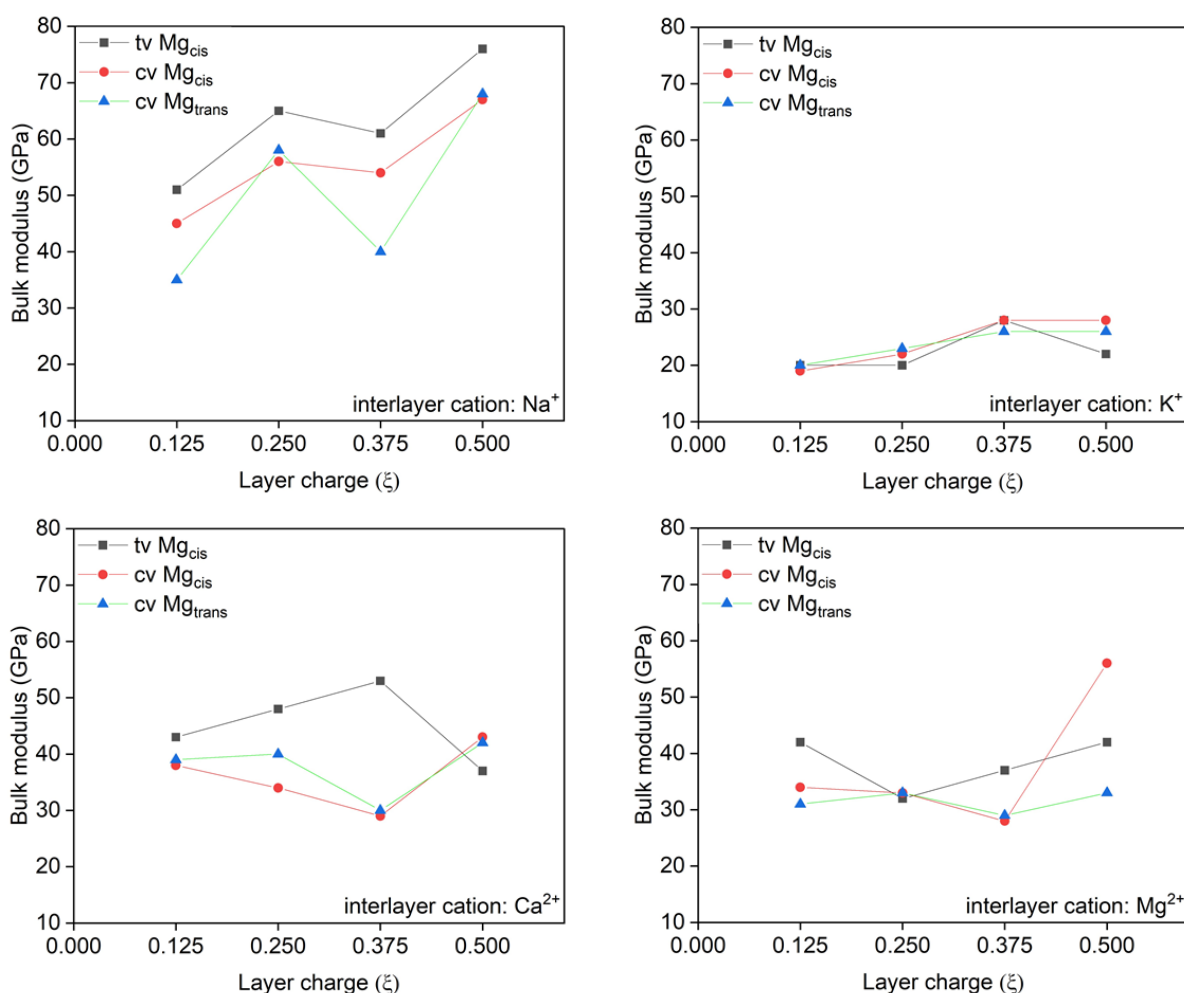


Figure 3.23: Bulk Modulus of saturated montmorillonite as function of layer charge

3.4 Summary, Conclusion and Future Outlook

3.4.1 Summary

The study examined the structural, energetic, and mechanical properties of Na^+ -, K^+ -, Ca^{2+} -, and Mg^{2+} -saturated montmorillonites using DFT-D3 calculations. The optimized structures revealed that Na^+ and K^+ occupy similar interlayer positions near the tetrahedral holes, while Mg^{2+} substitution in the octahedral layer induces local negative charges that attract interlayer cations for charge balance.

The most stable configurations were determined by total energy minimization and depend on cation type, layer charge, and supercell orientation. Na^+ -saturated montmorillonite was generally more stable than K^+ -saturated montmorillonite, and Ca^{2+} -saturated montmorillonite was more stable than Mg^{2+} -saturated montmorillonite. Stability increased with larger Mg–Mg distances in octahedral layers.

Basal spacing (d_{001}) correlated with cation size: $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. Monovalent cations exhibited an increase in d_{001} with higher layer charge, while divalent cations showed a decrease due to stronger electrostatic binding. The 2:1 layer thickness remained nearly constant ($\sim 6.8 \text{ \AA}$), with cations positioned closer to negatively charged regions. Mg^{2+} tended to occupy basal oxygen rings, and the average distance of cations from the layer surface followed $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Na}^+ < \text{K}^+$.

OH group orientations depended on both octahedral charge and cation type, affecting hydrogen bonding and interlayer stability. The bulk modulus varied with interlayer cation: Na^+ -saturated structures exhibited the highest stiffness (35–75 GPa), K^+ -saturated the lowest (20–30 GPa), while Ca^{2+} and Mg^{2+} forms showed intermediate, relatively consistent values (~ 35 –40 GPa).

3.4.2 Conclusion

The computational analysis demonstrates that montmorillonite stability, interlayer spacing, and mechanical properties are strongly governed by the nature and valence of interlayer cations. Na^+ and Ca^{2+} confer higher structural stability, while K^+ induces greater interlayer expansion due to its larger ionic radius and weaker electrostatic interactions. Divalent cations enhance interlayer cohesion and reduce basal spacing, whereas monovalent cations promote expansion. Overall, the study confirms that electrostatic and dispersion forces, rather than ionic size alone, dictate the structural and elastic behaviour of homoionic saturated montmorillonites.

3.4.3 Future Outlook

Building upon these DFT-D3 insights into cation–montmorillonite interactions, several promising directions emerge for future research:

1. Environmental and Geochemical Applications. Understanding the structural and energetic effects of interlayer cations provides a foundation for predicting clay behaviour in natural and engineered systems. Future studies could integrate aqueous ion exchange dynamics, temperature–pressure effects, and pH-dependent stability to model real-world geochemical processes such as contaminant immobilization, radionuclide retention, and soil remediation.

2. Multiscale Modelling and Validation. While the present work offers atomic-scale precision, coupling DFT calculations with molecular dynamics (MD) or Monte Carlo simulations can extend insights to mesoscale swelling and hydration phenomena. Experimental validation using XRD, NMR, or AFM under controlled hydration states will also strengthen the reliability of predicted structural parameters and mechanical moduli.
3. Cation Mixtures and Competitive Exchange. Natural clays rarely contain single cation species. Future studies should explore mixed-cation systems (e.g., $\text{Na}^+/\text{Ca}^{2+}$ or $\text{K}^+/\text{Mg}^{2+}$) to assess competitive adsorption, site preference, and cooperative effects on interlayer structure and elasticity.
4. Hydration and Intercalation Dynamics. Extending the model to include explicit water layers or organic intercalants could reveal how hydration shells modify interlayer forces, swelling pressure, and transport properties—key factors in applications such as bentonite barriers, catalysis, and drug delivery matrices.
5. Mechanical Performance in Applied Contexts. The observed cation-dependent stiffness trends suggest potential for tuning mechanical resilience in clay-based composites. Further computational and experimental work could optimize montmorillonite systems for reinforced polymer nanocomposites, ceramic precursors, or geotechnical materials requiring specific elastic responses.
6. Electronic and Surface Properties. Future DFT investigations incorporating charge density analysis or band structure calculations may clarify how interlayer cations influence surface reactivity, electron localization, and adsorption potential for polar molecules or pollutants.

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4 Position and Mobility of Interlayer Cation (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) in Saturated and Hydrated Montmorillonite

4.1 Introduction

The rate of ions moves through a solid can be understood in terms of the mechanism for the ions movement or ions migration and the activation energy barrier that encounter by the ions as ions move. Low-energy barriers that ions have to cross while moving can increase the mobility of ions to move from site to site. Low charge and small radii also increase the mobility of ions. More highly charge develop stronger electrostatic interaction and ions are less mobile (Atkins et al., 2010).

Chemistry and crystal structure heterogeneity are typical of montmorillonite, with as many as 96 structural variations proposed for the montmorillonite–beidellite series (Emmerich, 2009). This variation, coupled with different types of interlayer cations in natural samples, contributes to the heterogeneity in cation exchange, hydration, and swelling behaviour of montmorillonite and montmorillonite-rich materials such as bentonite. For these reasons, the structure of montmorillonite has been the subject of extensive research.

The structure and hydration process of montmorillonite have primarily been studied through X-ray diffraction (XRD) observations. In the following decades, advancements in techniques such as XRD, electron microscopy, thermal analysis, infrared (IR) spectroscopy, and various other spectroscopy methods have provided deeper insights into montmorillonite's crystal structure (Grim et. al., 1961; Greene-Kelly, 1957; Lanson, 2011; Drits and Tchoubar, 1990), classification (Emmerich et al., 2009; Grim and Kulbicki, 1961), and the influence of different parameters on its hydration and ion exchange processes (Ferrage, 2016; Ferrage, 2005; Wolters et al., 2007; Wolters et al., 2009; Moore and Reynolds, 1997; Sakharov et al., 1982; Lagaly and Weiss, 1969; Dzene et al., 2016; Tertre et al., 2011).

Despite extensive research on montmorillonite, several key questions remain unresolved, primarily due to the inherent structural and physicochemical heterogeneities of this mineral. One major question is the hydration process of montmorillonite; indeed, hydration begins with the hydration of interlayer cations, leading to the sequential formation of water layers within the interlayer, resulting in the 1W, 2W, and 3W states as water activity increases (Ferrage, 2016; Laird, 1996). This crystalline swelling is reflected by an increase in the unit cell parameter c (i.e., d_{001}) from approximately 11 to 19.5 Å. However, these values are not fixed and vary significantly depending on montmorillonite structure as well as environmental conditions like relative humidity, temperature, and pressure (Ferrage, 2016; Cases, 1997; Bérend et al., 1995).

The mobility and hydration of interlayer cations are closely related to their specific positions and interactions with the clay layers. These interactions are often assessed through experimental techniques such as electrical conductivity measurements, thermogravimetric and calorimetric analysis, CEC tests, XRD, and gravimetric sorption techniques (Ferrage, 2016; Dzene et al., 2016; Salle, et al., 2008; Ferrage, 2005; Haouzi et al., 2004; Liu et al., 2003; Zabat and Van Damme, 2000). These methods typically express cation behaviour in terms of activation energy for mobility, ion exchange, or hydration energy. However, the theoretical models used to derive these energies often fail to fully account for the complexities introduced by montmorillonite's structural heterogeneity, the nature of interlayer cations, and the distribution of layer charges. Compounding these challenges is the difficulty in obtaining a pure montmorillonite sample with 100% of a single interlayer cation from natural sources (Steudel and Emmerich, 2013) making it even more challenging to achieve accurate and consistent results.

The interlayer space and the hexagonal cavities on the surface of the layers provide pathways for ion diffusion and exchange. The specific pathways and mobility of ions are influenced by factors like the size and charge of the ions, the hydration state of the ions, and the specific characteristics of the smectite (e.g., the type and location of isomorphic substitutions). Ionic mobility and hydration energies are influenced by the type of interlayer cation and the presence of water. The type of cation in the interlayer significantly affects both hydration energy and mobility. Smaller cations tend to be more strongly hydrated, meaning they have a greater number of water molecules associated with them, leading to lower mobility. Larger cations have weaker hydration and higher mobility. Ionic mobility is inversely related to hydration energy. The amount of water present affects the hydration state of the clay and the mobility of ions.

Crystal structure, energy mapping and ion mobility pathways are interconnected concepts relevant to understanding ion transport in materials. Energy mapping in crystal structure is a visual representation of the potential energy experienced by atoms in a crystal structure as they move or change position. It illustrates how energy changes depending on the location of atoms in the crystal. A crystal structure is an orderly arrangement of atoms in a solid. Potential energy is the energy stored in a system due to its position. Energy mapping is a visual representation of potential energy as a function of position. Energy maps can be interpreted by looking at the position of the lowest points on the energy map (minimum energy), which indicate the most stable positions for atoms in the crystal. Activation energy is the increase in energy required for an atom to move from one position to another. The curvature of the energy map shows how easily atoms can move or vibrate in that position. Energy maps consider the movement of atoms on a small scale (thermal vibrations). Crystal structure mapping helps to understand the stability, properties, and behaviour of crystalline materials.

Ion mobility pathways in crystal structures, particularly relevant in battery materials, refer to the route of ions take through the material's lattice during ion transport. These pathways are crucial for determining a material's suitability as a solid electrolyte or electrode, influencing factors like conductivity and energy density. Understanding and optimizing these pathways is key to developing high-performance batteries. Ion mobility describes how easily ions move within a material. Pathways are the specific routes ions take as they move from one location to another within the crystal lattice. The calculated potential energy surface reveals the energy barriers along the pathway, influencing the ease of ion movement. Energy barriers are crucial for determining ion mobility which lower barriers indicate easier movement. Factors influencing barriers are ion size, charge, and the chemical

environment (e.g., electronegativity of surrounding atoms) affect the migration barrier. The energy landscape (derived from energy mapping) directly influences ion mobility. Lower energy barriers correspond to higher ion mobility.

The main focus of this study is to compare and analyse the position of cation, energy mapping and ionic mobility of interlayer cation (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) in homoionic saturated montmorillonite structure for each octahedral structure. The study was restricted to saturated montmorillonite structures with layer charge (ξ) = 0.500. Using a dispersion-corrected DFT-D3 approach, this research aims to identify the most stable structural configurations and quantify the energetic barriers associated with cation movement across different octahedral configurations. The findings will provide deeper insight into the structure–energy–mobility relationship in montmorillonite and contribute to a more comprehensive understanding of ion transport mechanisms in homoionic saturated montmorillonite.

4.2 Methods

4.2.1 Model Structure

The structural model used is as described in section 2.1.1.

4.2.2 Total Energy Distribution

The determined of total energy distribution in simplest Na^+ , K^+ , Ca^{2+} dan Mg^{2+} -saturated homoionic montmorillonite structures and ion mobility of each interlayer cation are described in section 2.1.3.

4.2.3 Computational Chemistry Method

The parameters used in the Computational Chemistry Method, the software used, and the parameters of the atoms involved in homoionic saturated montmorillonite structures are described in section 2.1.5.

4.3 Results and Discussion

This section presents the computational and structural analysis of homoionic saturated montmorillonite, examining how cation type, structural configuration, and hydration influence its stability and ion mobility. Energy mapping (E-Map) is used to visualize total energy distributions and preferred cation positions within different octahedral configurations ($tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$, and $cv \text{ Mg}_{trans}$). Energy barriers between stable lattice sites are evaluated to assess ionic migration pathways. Additional simulations explore the effect of water molecules on ion mobility and interlayer interactions by mitigating Coulombic attraction and modifying hydration dynamics. Finally, the mechanisms of hydration and swelling are discussed to explain how structural charge distribution, cation valence, and water content collectively govern the physicochemical behaviour of homoionic saturated montmorillonite.

4.3.1 Energy mapping (E-Map) of Cation Distribution in Homoionic Saturated Montmorillonite

The energy mapping (E-Map) for Na^+ -saturated montmorillonite represented the Total Energy (eV) distribution the structure with different position of cation in interlayer. Blue-coloured areas are the areas that can be occupied by Na^+ ions with high probability and stability. Blue areas have relatively smaller total energy compared to other coloured areas, such as green, yellow and orange areas (Figure 4.1, 4.2, 4.3 and 4.4). In each $tv \text{ Mg}_{cis}$, $cv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ structures, each E-Map has four blue regions. The sharpness of the blue colour intensity in the $cv \text{ Mg}_{trans}$ structure is higher than $tv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{cis}$ this indicated by the minimum total energy. The Total Energy (eV) of $cv \text{ Mg}_{trans}$ structure is lower than $tv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{cis}$ structure. The sharpness of the blue colour intensity on E-map correlated with the stability of these structure and indicates that the $cv \text{ Mg}_{trans}$ Na^+ -saturated montmorillonite structure is more stable than $tv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{cis}$ structure. Different with Na^+ -saturated montmorillonite, $cv \text{ Mg}_{cis}$ K^+ -saturated montmorillonite structure is more stable than $tv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ structure (Figure 4.1 and 4.2). For divalent cation, $cv \text{ Mg}_{cis}$ is more stable $tv \text{ Mg}_{cis}$ and $cv \text{ Mg}_{trans}$ in both of Ca^{2+} - and Mg^{2+} -saturated montmorillonite (Figure 4.3 and 4.4).

From the four figures, the behaviour of divalent cations versus monovalent cations in an E-Map, where the uneven blue distribution on the divalent E-Map suggests their concentrated placement within the interlayer due to the influence of two substitutions in the concentrated octahedral sheet, these substitutions likely create localized regions of higher negative charge within the octahedral sheet. This unevenness indicates that divalent cations, carrying a higher charge (two positive charges) compared to monovalent cations (one positive charge), are more strongly influenced by localized structural features, such as charged sites within the interlayer and octahedral sheet, leading to a preference for specific areas. Divalent cations possess a +2 charge, whereas monovalent cations have a +1 charge. This stronger positive charge makes them more attracted to negatively charged sites within the crystal structure. The higher charge of the divalent cation causes it to be more strongly attracted to these negatively charged sites. This strong attraction leads to a more uneven distribution of divalent cations in the interlayer, as they preferentially bind to these specific, highly charged locations. In contrast, monovalent cations have a weaker charge and, therefore, a less pronounced attraction to these specific sites. Their distribution on the E-Map is likely more diffuse or "territorial," showing a broader, more even spread across the interlayer.

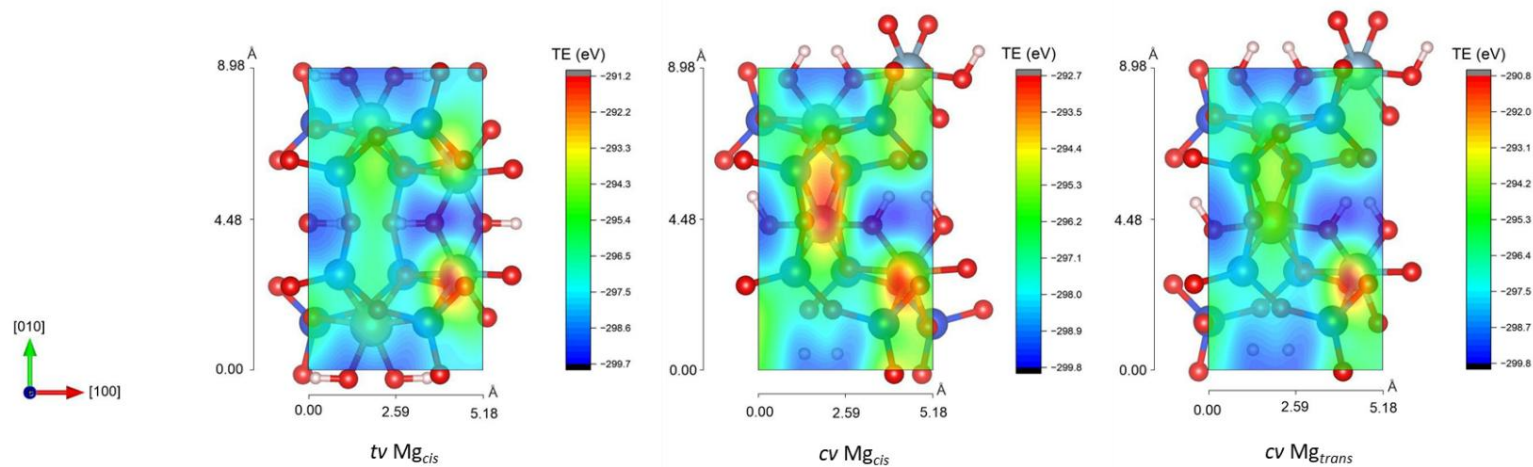


Figure 4.1: Energy Mapping Na^+ -saturated montmorillonite 1UC and $\xi = 0.500$

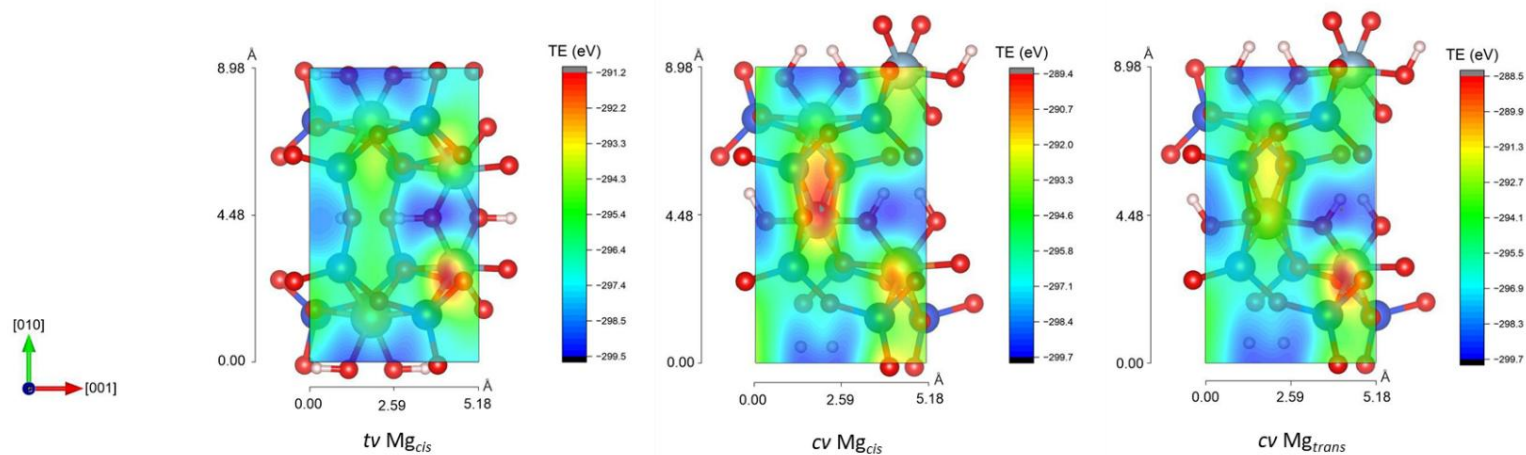


Figure 4.2: Energy Mapping K^+ -saturated montmorillonite 1UC and $\xi = 0.500$

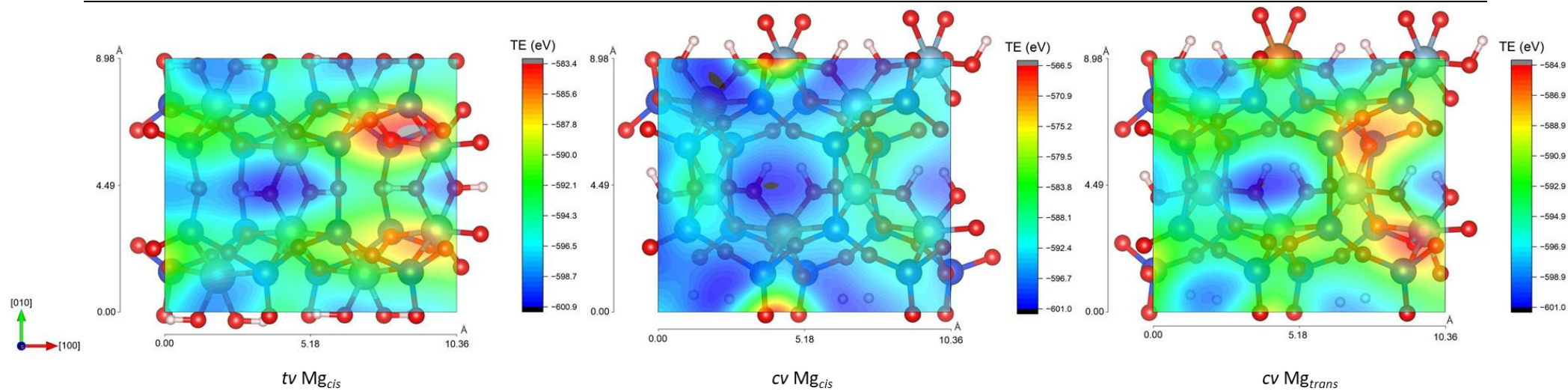


Figure 4.3: Energy Mapping Ca^{2+} -saturated montmorillonite 2UC and $\xi = 0.500$

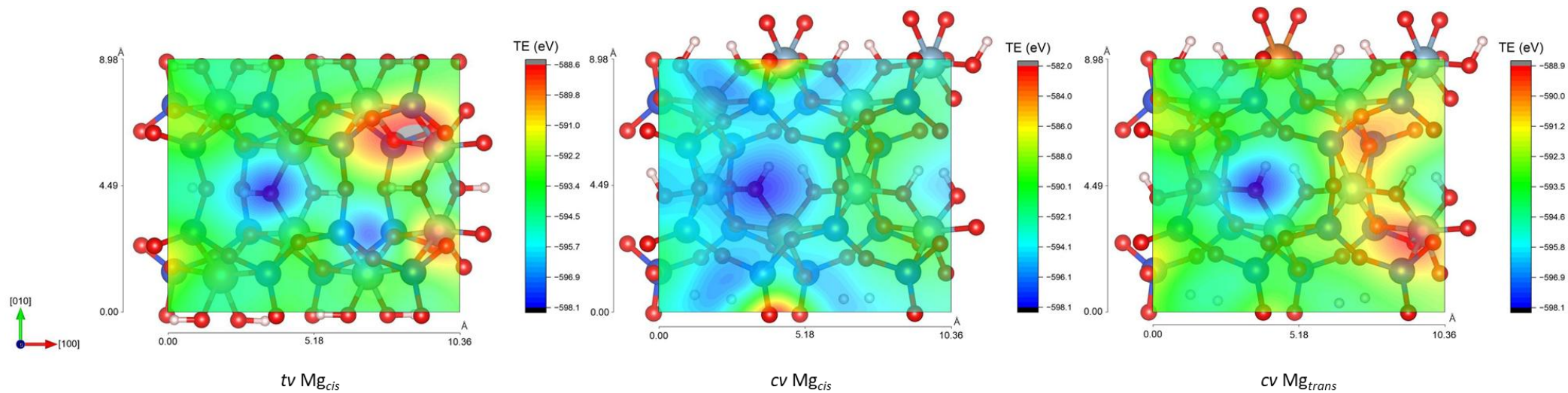


Figure 4.4: Energy Mapping Mg^{2+} -saturated montmorillonite 2UC and $\xi = 0.500$

4.3.2 Ionic Mobility Pathways and Energy Barriers

The line passing through points A-B-C-D is the first pathways and points A'-B'-C'-D' is the second pathways of Na^+ mobility for $\text{tv Mg}_{\text{cis}}$. the barrier passed by Na^+ through first pathways is higher than the second pathway, this indicated that Na^+ movement easier through the second pathway. The same thing also occurs in the $\text{cv Mg}_{\text{cis}}$ and $\text{cv Mg}_{\text{trans}}$ structures. For Na-saturated montmorillonite, ion mobility in the $\text{cv Mg}_{\text{cis}}$ structure is higher than in $\text{tv Mg}_{\text{cis}}$ dan $\text{cv Mg}_{\text{trans}}$ in both recommended pathways. In contrast with Na^+ -saturated montmorillonite, overall ion mobility in $\text{tv Mg}_{\text{cis}}$ K^+ -saturated montmorillonite higher than $\text{cv Mg}_{\text{cis}}$ and $\text{cv Mg}_{\text{trans}}$ structures in both recommended pathways. The barrier passed by K^+ in $\text{tv Mg}_{\text{cis}}$ structure lower than $\text{cv Mg}_{\text{cis}}$ and $\text{cv Mg}_{\text{trans}}$ structures (Figure 4.5 and 4.6).

In divalent cations (Figures 4.7 and 4.8), it is observed that the blue areas (indicating areas of high stability) are not evenly distributed throughout the crystal lattice area as in monovalent cations. This is because the distribution of two Mg substitutions in the octahedral layer is concentrated in one place, so that the more negatively charged areas are not evenly distributed throughout the crystal lattice plane. At a glance, these uneven blue areas cause an uneven energy barrier that is greater than the energy barrier in the lattice of monovalent cations. In the structure for Ca^{2+} and Mg^{2+} -saturated montmorillonite, there is a very high energy barrier jump in the second pathway (E'-F'-G'-E'). The figure shows that the high energy barrier is caused by the cation passing through the red area as it moves from one point to another. From all the images and results obtained based on the energy barrier that must be overcome by each cation to move, it can be concluded that the order of ionic mobility in saturated montmorillonite is $\text{Na} > \text{K} > \text{Mg} > \text{Ca}$.

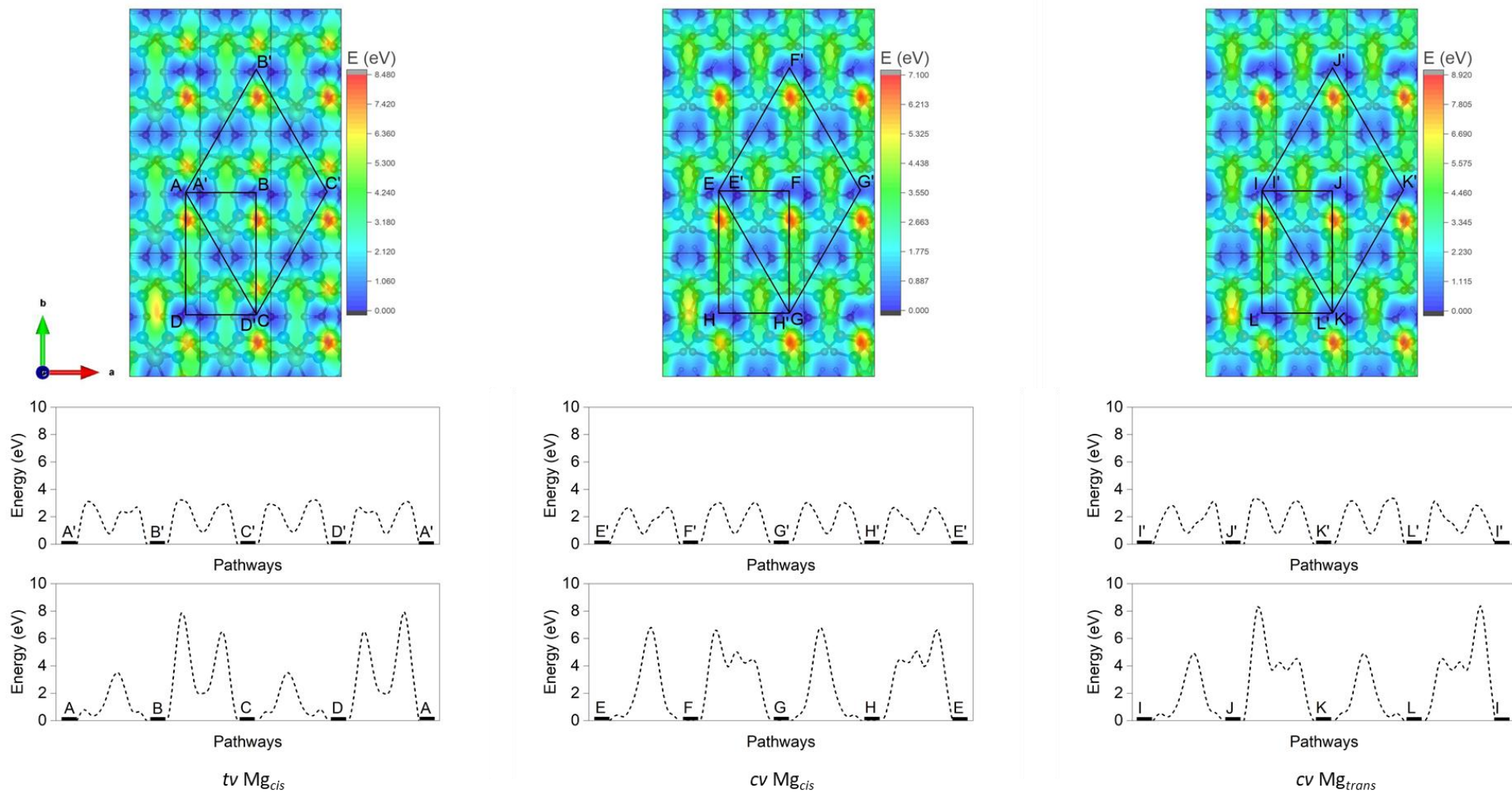


Figure 4.5: Ionic mobility pathways and Energy Gap of Na^+ -saturated montmorillonite 1UC and $\xi = 0.500$

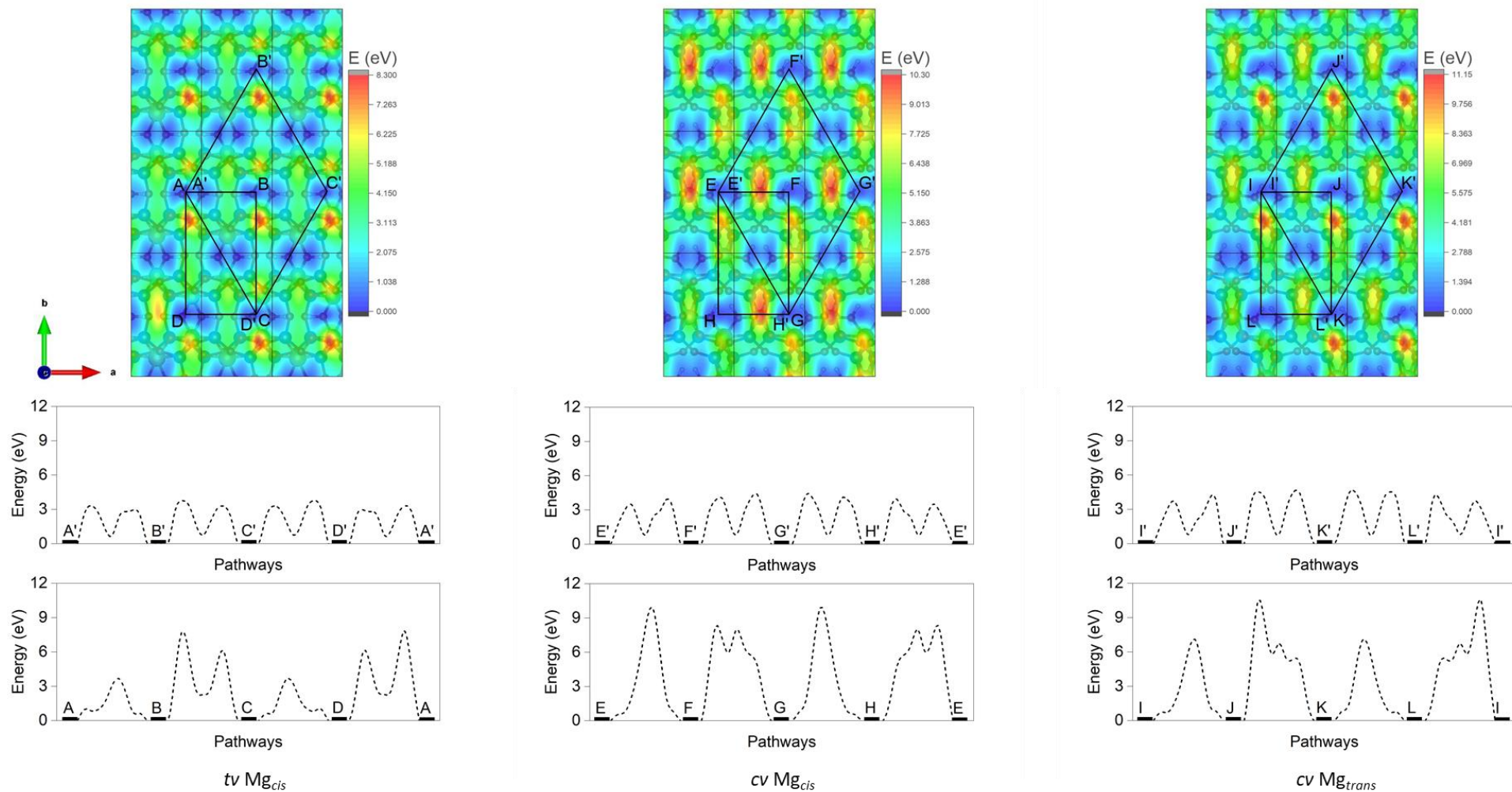


Figure 4.6: Ionic mobility pathways and Energy Gap of K^+ -saturated montmorillonite 1UC and $\xi = 0.500$

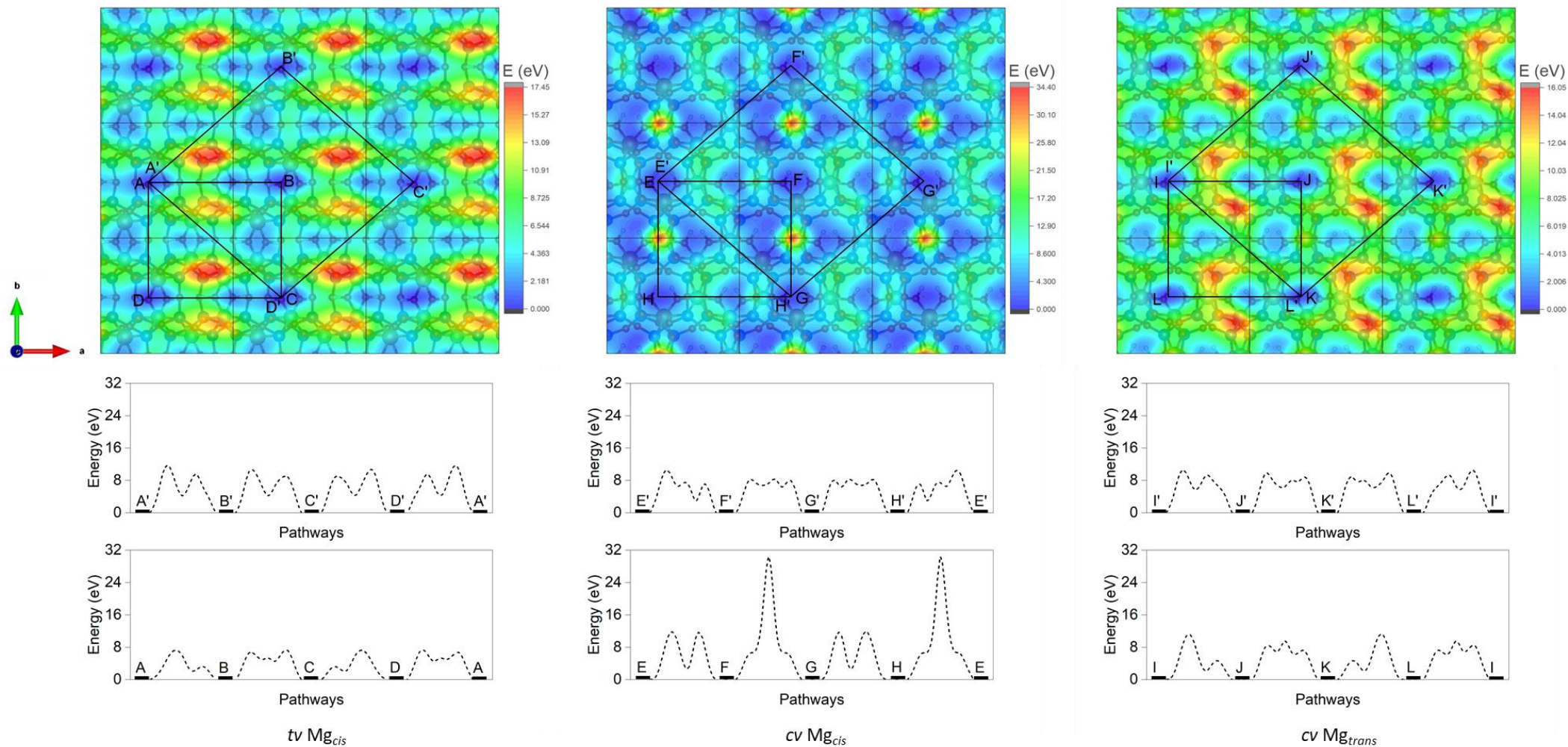


Figure 4.7: Ionic mobility pathways and Energy Gap of Ca^{2+} -saturated montmorillonite 2UC and $\xi = 0.500$

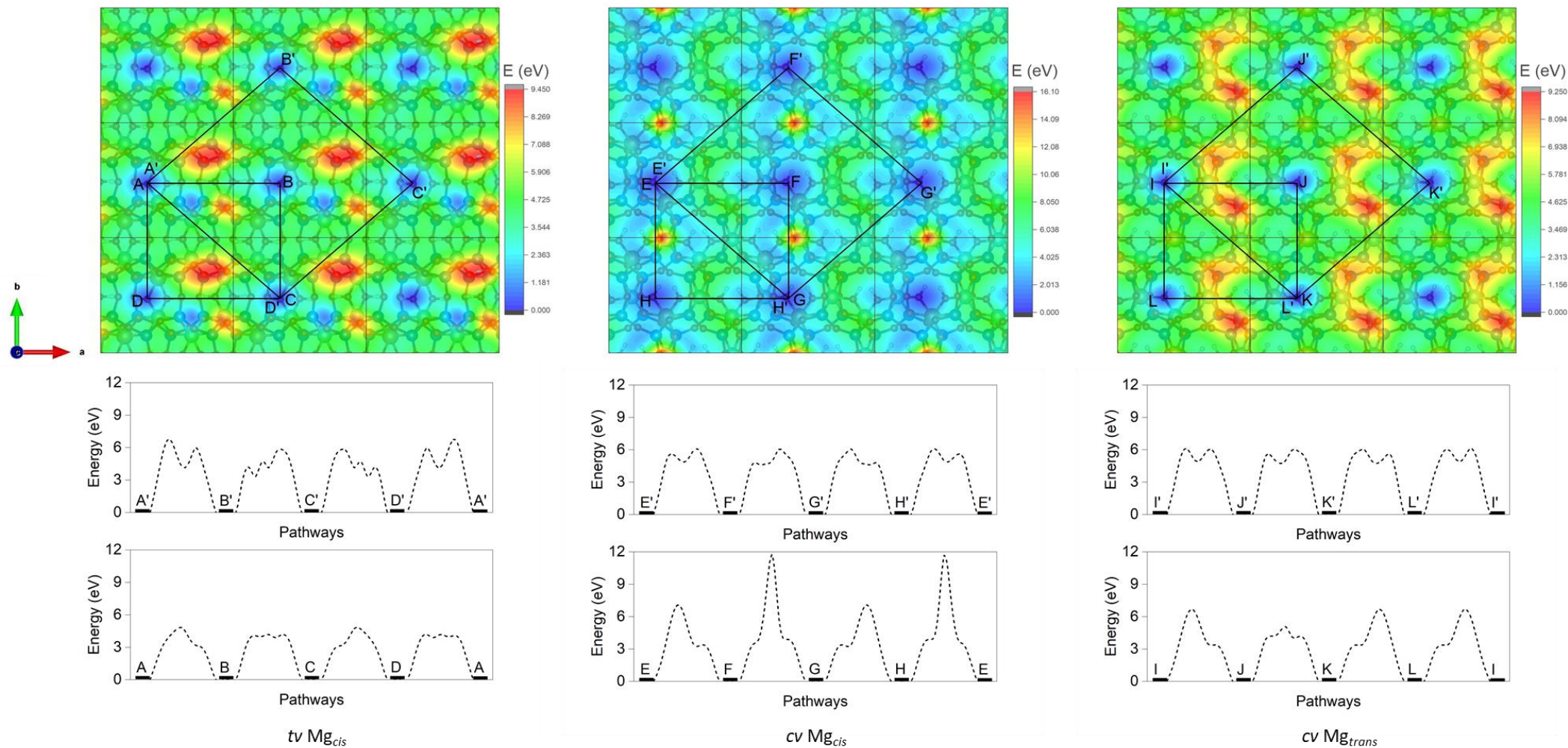


Figure 4.8: Ionic mobility pathways and Energy Gap of Mg^{2+} -saturated montmorillonite 2UC and $\xi = 0.500$

4.3.3 Influence of Water Molecules on Ionic Mobility

Figure 4.9 is a simulation image to determine the effect of water molecules on ion mobility. This simulation is limited to Na^+ and K^+ montmorillonite to simplify calculations and reduce interference from uneven negative areas in the cell unit. Starting point, A is the point where the cation occupies the most stable position and then moves to point B by passing through an intermediate position. The A-B pathway and other pathways can be seen more clearly in Figures 4.10 and 4.11.

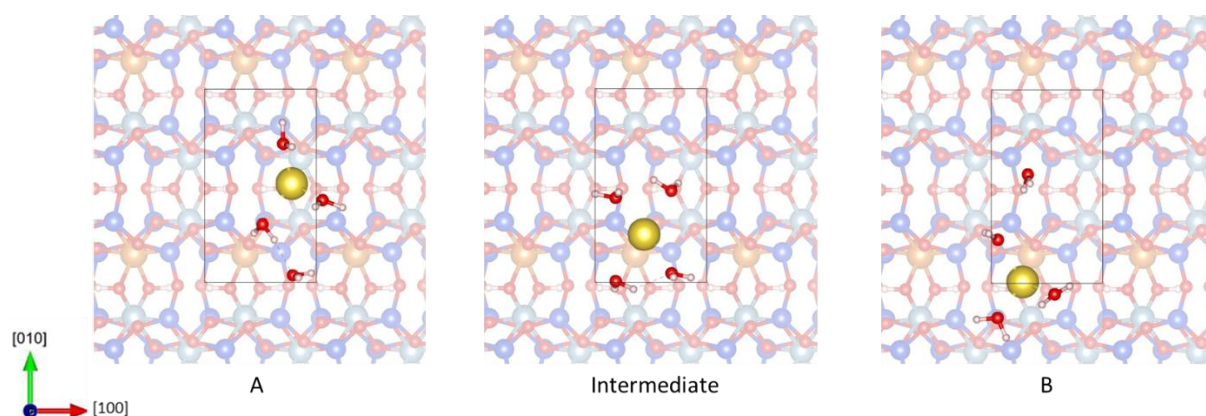


Figure 4.9: Position of Na^+ (hydrated) and water molecules in *tv* Mg_{cis} Na^+ -Montmorillonite 1UC and $\xi = 0.500$

Figure 4.9 shows that water molecules move dynamically, influenced by interactions between water molecules and the 2:1 layer surface at certain points. Figures 4.10 and 4.11 clearly show that the presence of water can reduce the energy gap that inhibits ion movement in the montmorillonite structure. the presence of water reduces the energy barrier for ion movement in montmorillonite by reducing the Coulombic interactions between ions and the negatively charged clay layers. Water molecules enter the interlayer spaces, forming hydration layers and diffuse aqueous layers around the ions, weakening the electrostatic attraction that otherwise restricts ion mobility. This process allows for increased diffusion and exchange of ions within the montmorillonite structure, a key aspect of its swelling and hydration behaviours. This is indicated that when Na^+ or K^+ ion is hydrated, the presence of water molecules surrounding Na^+ or K^+ ions reduce the interaction between Na^+ or K^+ ion and the clay surface. The interaction between Na^+ or K^+ ions and water molecules are stronger than the interaction between positively charged Na^+ or K^+ with a negatively charged clay surface. Hydrated Na^+ or K^+ ion can move more easily compared to non-hydrated Na^+ or K^+ ions.

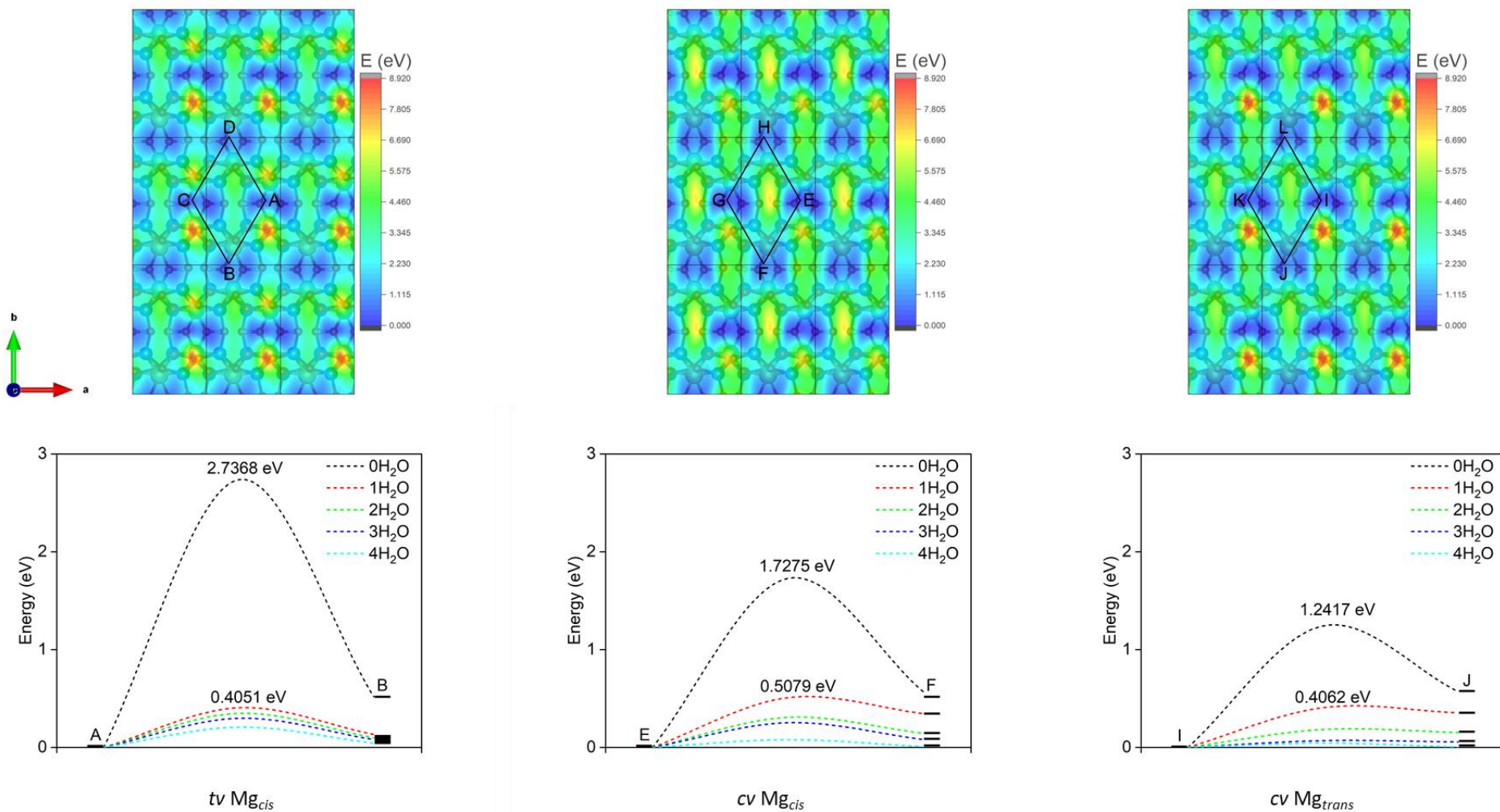


Figure 4.10: Energy gap of ionic mobility of Na^+

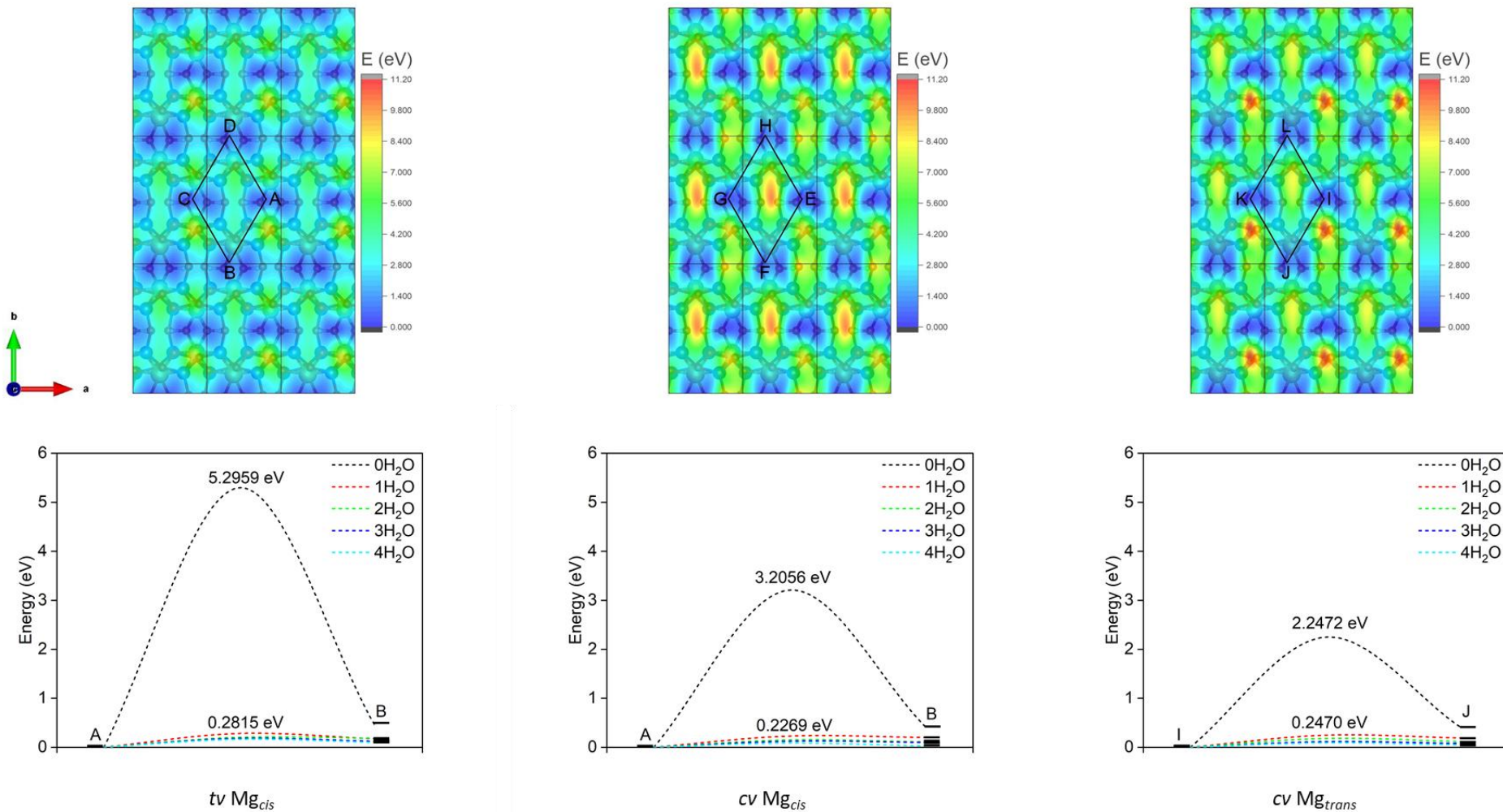


Figure 4.11: Energy gap of ionic mobility of K^+

Figure 4.12 shows the energy gap of Na^+ and K^+ ion mobility as a function of the number of water molecules. The addition of water molecules significantly reduces the energy gap, and the continuous addition of water molecules can produce a straight line that approaches an energy gap of zero. The electrostatic interaction between cation interlayer and water molecules is a crucial factor retarding the diffusion of interlayer water, which in turn affects the ionic mobility of cation interlayer. In Na-montmorillonite with high water contents, the interlayer Na^+ ion moves relatively free way (Zhang, et al., 2014).

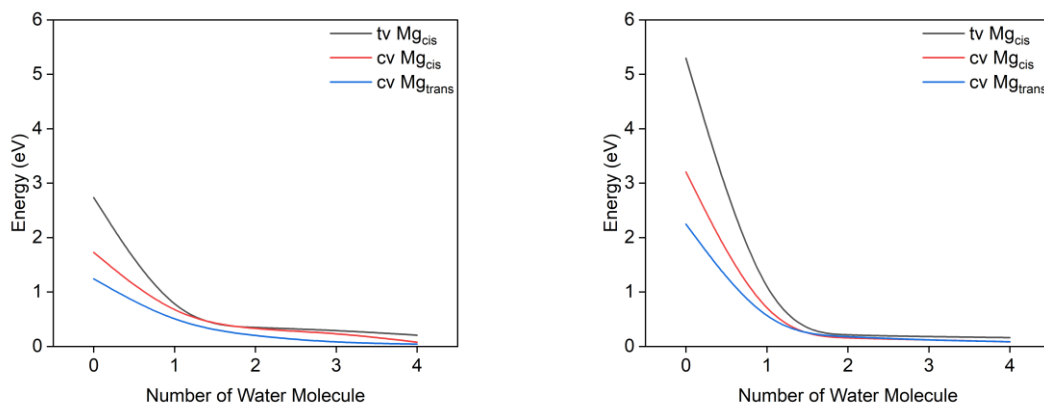


Figure 4.12: Energy gap of ionic mobility of Na^+ and K^+ as function of number of water molecules

The hydration process of montmorillonite involves water molecules being attracted to the negatively charged silicate layers of the clay, initially adhering to its outer surface due to electrostatic forces, which then allows them to diffuse into the spaces between layers. low-valent cations such as Mg^{2+} or Fe^{2+} can substitute Al^{3+} in the octahedral sheet, creating a permanent negative charge in the Al-octahedral sheet. These negative charges are neutralized by interlayer cations like Na^+ or Ca^{2+} , which generate an electrostatic field. This combined electrical field from the tetrahedral and octahedral layers attracts water molecules and other cations, leading to their adsorption onto the montmorillonite surface and their subsequent movement into the interlayer spaces. Water enters Montmorillonite via two main swelling processes: first, by forming discrete water layers within the interlayer spaces due to cation-water interactions (crystalline swelling), and second, by the separation of particles from each other in a more substantial, osmotic process driven by cation imbalances. Both hydration mechanisms are influenced by the type of interlayer cation, the overall charge of the clay layers, and the resulting forces between them. Montmorillonite crystals swell and adsorb cations readily because their oxygen-terminated surfaces lack hydrogen bonding, instead being held by weak intermolecular forces, creating large spacing that allows water entry and swelling. These montmorillonite crystals also have a highly negative charge and strong ion exchange capacity due to significant lattice substitution, enabling them to attract and hold more cations (Al-Zaoari et al., 2022; Du, et al., 2023; Zhou et al., 2025; Li, et al., 2024).

Montmorillonite has a permanent negative charge on its silicate layers, which is balanced by interlayer exchangeable cations. Water molecules, being polar, are attracted to these charged surfaces and ions. Water molecules form hydration shells around the ions, creating a diffuse aqueous layer. This effectively increases the distance between the ion and the negatively charged clay surface. The

increased separation and shielding by water molecules significantly weaken the strong electrostatic (Coulombic) attraction that would otherwise hold the cations tightly to the clay surfaces. With the reduced Coulombic inhibition, cations can more easily move from inner-sphere complexes (where they are strongly bound to the surface) to outer-sphere complexes or even into the diffuse aqueous layer, enabling their exchange within the montmorillonite structure.

4.4 Summary, Conclusion and Future Outlook

4.4.1 Summary

Energy mapping (E-Map) revealed the distribution of total energy within Na^+ -, K^+ -, Ca^{2+} -, and Mg^{2+} -saturated montmorillonite structures. Blue regions represented stable cation positions with low total energy. Among Na^+ -saturated structures, *cv* Mg_{trans} was the most stable, while in K^+ -saturated montmorillonite forms, *cv* Mg_{cis} showed greater stability. For divalent cations (Ca^{2+} and Mg^{2+}), *cv* Mg_{cis} was again the most stable.

The E-Maps of divalent cations displayed uneven blue areas, reflecting their stronger localization near highly charged regions within the octahedral layer due to their +2 charge. In contrast, monovalent cations were more evenly distributed, indicating weaker electrostatic binding and higher mobility.

Ionic mobility analysis showed that ions move by overcoming energy barriers between stable lattice positions. Na^+ exhibited the lowest migration barriers (highest mobility), followed by K^+ , Mg^{2+} , and Ca^{2+} . For Na^+ -saturated montmorillonite, *cv* Mg_{cis} offered easier ion movement, while in K^+ -saturated montmorillonite, *tv* Mg_{cis} favored greater mobility. Divalent cations experienced higher and more irregular energy barriers due to localized negative charge concentrations.

Simulations including water molecules demonstrated that hydration significantly reduces energy barriers for ion movement. Water molecules form hydration shells that weaken Coulombic attraction between cations and the negatively charged clay layers, allowing ions to diffuse more freely. Increasing water content progressively decreases the energy gap, approaching near-zero values, indicating almost unhindered cation motion at high hydration levels.

4.4.2 Conclusion

The energy mapping and mobility analyses show that montmorillonite stability and ion dynamics depend strongly on cation charge, type, and hydration. Monovalent cations (Na^+ , K^+) exhibit more uniform energy distributions and higher mobility, while divalent cations (Ca^{2+} , Mg^{2+}) are more localized and less mobile due to stronger electrostatic binding. Hydration dramatically enhances ionic mobility by reducing electrostatic interactions and enabling diffusion within the interlayer. Overall, the order of ionic mobility in montmorillonite is: $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$, and hydration plays a crucial role in facilitating ion exchange and swelling behaviour in the homoionic saturated montmorillonite structure.

4.4.3 Future Outlook

The present energy-mapping and ion-mobility analysis provides a detailed understanding of how cation type, charge, and hydration govern the energetic landscape and diffusion behaviour in montmorillonite. Building on these insights, several research directions can be pursued to deepen both the theoretical and practical understanding of ion–clay interactions:

1. **Dynamic Hydration Studies.** Future work should investigate time-dependent hydration processes to capture the evolution of cation mobility under varying humidity, temperature, and pressure. Combining *ab initio* molecular dynamics with grand canonical Monte Carlo simulations could reveal how hydration shells reorganize dynamically and influence ion-exchange kinetics.
2. **Mixed-Cation and Natural Clay Systems.** Since natural montmorillonites often contain mixed interlayer cations, extending the E-Map approach to multi-cation systems (e.g., $\text{Na}^+/\text{Ca}^{2+}$ or $\text{K}^+/\text{Mg}^{2+}$ mixtures) would help clarify competitive ion migration and exchange behaviour—key to understanding soil chemistry, contaminant transport, and water softening processes.
3. **Temperature-Dependent Mobility.** Investigating the thermal activation of cation diffusion could establish quantitative relationships between migration barriers and temperature, allowing prediction of ion transport in geological environments or engineered barriers under thermal gradients.
4. **Applications in Environmental and Energy Systems.** Insights from this study could guide the design of efficient ion-exchange materials, bentonite barriers for nuclear waste repositories, and electrochemical systems (e.g., clay-based membranes or electrodes) where controlled ionic transport is critical. Tailoring interlayer chemistry and hydration conditions could enable optimization of selective ion retention, swelling control, and ionic conductivity.
6. **Machine Learning and Predictive Modelling.** The E-Map datasets can be leveraged to develop machine learning models that predict energy landscapes and ion mobility for various cation types or montmorillonite compositions, accelerating the screening of materials for targeted properties without exhaustive DFT calculations.

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5 Influence of Cation and Layer Charge on Hydration of Homoionic Saturated Montmorillonite

5.1 Introduction

Montmorillonite is a phyllosilicate clay mineral with a fundamental 2:1 layered structure, consisting of two tetrahedral silica sheets sandwiching a central octahedral alumina sheet. This structure is characterized by a permanent negative charge, primarily from the isomorphic substitution of lower-valence cations (e.g., Mg^{2+} for Al^{3+}) in the octahedral layer. These negative sites attract cations, which reside in the interlayer space along with water molecules, a region that dictates physical properties of montmorillonite and behaviour. Hydration, the process by which water molecules interact with the montmorillonite interlayer, leads to the swelling of the clay structure. DFT is a quantum-mechanical method used to model the complex interactions between water molecules, interlayer cations, and the Montmorillonite framework at an atomic and electronic level. This approach allows for the detailed investigation of structural, energetic, and electronic properties of hydrated Montmorillonite, providing a theoretical basis for understanding experimental observations and the behaviour of clays in various environmental and technological applications.

The hydration and dehydration reactions of montmorillonite are important in many geological processes and have been linked to phenomena as diverse as sediment over pressurization and petroleum migration (Berghout et al., 2010). Characterized by significant swelling capacities, montmorillonites are used widely for the intercalation of various species, from small molecules to polymers, into the interlayer space (Kato and Usuki, 2000). The design of new clay-polymer nanocomposites with improved mechanical (Liu et al., 2003; Wan et al., 2003; Zhang et al., 2005), heat resistant (Qin et al., 2003), or coating (Majumdar et al., 2003) properties is a field of intense research. Clays are also used as molecular-sieve catalysts (Kantam et al., 1998), ion exchangers, and adsorbents (Manju, et al., 1999).

Numerous DFT studies investigate the influence of different interlayer cations (e.g., Li^+ , Na^+ , K^+ , Ca^{2+}) on Montmorillonite hydration. These studies demonstrate that the type and number of water molecules and cations in the interlayer significantly impact the basal spacing of Montmorillonite (d_{001}), adsorption energies, and overall stability. Extensive DFT research focused on characterizing water-cation-Montmorillonite interactions at the (001) basal plane, revealing how cation type and concentration influence hydration, stability, and ion mobility, providing insights into montmorillonite adsorption mechanisms and macroscopic behaviour. There have been several theoretical investigations on the hydration of clay minerals with more developed DFT methods, considering both static and dynamic conditions (Mignon et al., 2009; Churakov 2013; Yang et al., 2017; Chatterjee 2005; Pirillo et al. 2015). DFT studies in montmorillonite hydration are mostly devoted to the description of the interlayer hydration, and only a few considered the mineral surfaces and edges (Martins et al.,

2014; Ulian et al., 2021). DFT has been widely used in simulating electronic properties and reactivity of crystals, surfaces, and molecules. The DFT method is also often used to study the hydration, adsorption, plasticity, electronic and mechanical properties of clay minerals (Ertan et al., 2017; Scholtzová and Tunega, 2020; Min et al., 2022; Chen et al., 2019; Peng et al., 2016; Han et al. 2016; Peng et al., 2017; Peng et al., 2018 and Kasprzhitskii, 2016).

DFT calculations in montmorillonite reveal stable water and cation configurations within its interlayer, with hydration reducing energy barriers for cation migration and increasing ion mobility. Furthermore, DFT quantifies bulk modulus of montmorillonite, showing how its mechanical properties vary with the level of hydration. A theoretical study using DFT investigated how single water molecules interact with Na-montmorillonite surfaces, finding that water adsorbs via electrostatic attraction to Na⁺ on the basal (001) surface and through hydrogen bonds with surface hydroxyl groups on the edge (010) surface. The (010) surface had a stronger adsorption energy, and in both cases, some electron transfer occurred from the clay to the water molecule, indicating a significant interaction in the hydration process, which is vital for many applications involving clay minerals. Under the same number of water molecules, the interlayer spacing of Na-montmorillonite increases slowly. After high-temperature dehydration, the interlayer spacing change of Na-montmorillonite is small.

In the water-saturated state, the interlayer spacing of Na-montmorillonite is larger than that of Ca-montmorillonite. High-temperature removal of interlayer water has a small effect on the interlayer spacing of kaolinite. The thickness of the surface hydration film and the degree of hydration of Ca-montmorillonite are greater than those of Na-montmorillonite. The thickness of the surface hydration film of kaolinite (001) is greater than that of kaolinite (001), and the thickness of the surface hydration film and the degree of hydration of kaolinite are less than those of montmorillonite. The higher water absorption rate of Na-montmorillonite interlayers is the main reason for its higher water content than Ca-montmorillonite (Zhang et al., 2025). DFT provides a foundational atomic-level understanding of montmorillonite behaviour by analysing electron distributions, which helps explain its macroscopic properties like swelling and temperature response. By examining charge density distributions and electron localization, DFT reveals how cation adsorption and hydration alter MMT's mechanical and physical characteristics, allowing for better prediction and control of its behaviour in various engineering and environmental applications (Shafei et al., 2021). DFT studies of montmorillonite frequently use the (001) basal plane to understand interlayer hydration and water interaction because it's crucial for this property. These studies often employ periodic DFT calculations to simulate water adsorption at various concentrations, yielding detailed insights into the structural and energetic aspects of these interactions (Ulian, 2011). The (001) basal plane is central to understanding how water molecules interact and are held within the interlayer spaces of montmorillonite. This is a key feature for its swelling behaviour.

Clay-water interaction is a fundamental topic across many scientific fields, from material science and geotechnical engineering to soil science and the biosphere, because water is abundant and clay minerals are common, with water even being part of clay's structure. This interaction involves various physical forces like hydrogen bonds and van der Waals forces on the clay's surface and is the focus of this chapter, which reviews water structure, ion interactions, and the specific ways water interacts with clay minerals, including recent spectroscopic and modelling studies. Surface interactions include hydrogen bonding, ion–dipole, dipole–dipole, and van der Waals interactions involving both neutral and charged clay mineral surfaces. Recent spectroscopic and molecular modelling studies of clay

mineral–water interactions are presented in the framework of molecular probes and reporter groups (Johnston, 2018).

The main focus of this study is to investigate the effect of water molecules on saturated montmorillonite, changes in the structure and properties of saturated montmorillonite due to the addition of water molecules, and to study the hydration process. The study was restricted to saturated montmorillonite structures with layer charge (ξ) = 0.250 and 0.500.

5.2 Methods

5.2.1 Model Structure

The structural model used is as described in section 2.1.1.

5.2.2 Hydration of Homoionic Saturated Montmorillonite

The hydration modelling of Na^+ , K^+ , Ca^{2+} and Mg^{2+} -homoionic saturated montmorillonite are described in section 2.1.4.

5.2.3 Computational Chemistry Method

The parameters used in the Computational Chemistry Method, the software used, and the parameters of the atoms involved in Homoionic Saturated Montmorillonite Structures are described in section 2.1.5.

5.3 Results and Discussion

Density Functional Theory studies on smectite hydration demonstrate that DFT accurately predicts the stepwise swelling of smectites by quantifying the interlayer water molecules and their interaction with the clay structure. These studies identify the stable hydration states (e.g., monolayer, bilayer), the influence of different exchangeable cations on swelling and ion mobility, and the specific binding sites of cations within the interlayer. The findings provide detailed insights into the energetic and entropic factors driving swelling, revealing complex interactions between water, cations, and the charged smectite layers.

5.3.1 Stepwise Expansion of Basal Spacing with Increasing Hydration in Montmorillonite

The basal spacing of montmorillonite increases in a stepwise manner with the number of water molecules per cation, as water molecules intercalate between the clay layers to form hydration shells around the cations and montmorillonite surface. The extent of this increase is dependent on factors like charge and size of cation; and layer charge of montmorillonite. The intrinsic negative charge of the montmorillonite structure attracts the positive cations and their hydration shells. A higher layer charge

generally leads to a greater ability to attract cations and water, potentially influencing the degree of swelling.

Figures 5.1 and 5.2 show d_{001} as a function of $H_2O/cation$ with $\xi = 0.250$ and 0.500 , respectively, for Na^+ , K^+ , Ca^{2+} , and Mg^{2+} -homoionic saturated montmorillonite. In general, for all montmorillonites, an increase in the number of water molecules per cation increases d_{001} . Water molecules are highly attracted to the exchangeable cations within the interlayer space of montmorillonite, forming hydration shells. As more water molecules enter the interlayer space, they further hydrate the cations, which pushes the layers of the montmorillonite apart, thus increasing the d_{001} basal spacing and causing the clay mineral to swell.

The increased amount of water reduces the interaction between cations and the montmorillonite surface, as the cation-water interaction is stronger than the cation-surface interaction. As the amount of water increases in contact with montmorillonite, the strong cation-water interactions lead to the hydration and solvation of the interlayer cations. The higher water content makes exchangeable cations have a stronger driving force for the swelling of montmorillonite, but it causes adverse effect on the contribution of cations to the total driving force Peng, et.al (2019). For swelling clays, the distance between the layers increases with increasing water content as a result of crystalline swelling.

Cations surrounded by water molecules during the hydration process stabilize ions in the interlayer and prevent cations from interacting strongly with the montmorillonite surface. Water molecules form a hydration shell around interlayer cations in montmorillonite, which stabilizes the ions and increases the interlayer spacing, thereby preventing direct, strong electrostatic interaction between the cations and the negatively charged montmorillonite surface. More water molecules around a cation increase the layer spacing (d_{001}) because the stronger cation-water bonds reduce the cation's interaction with the clay surface. Adding more water molecules around a cation can increase the interlayer spacing (d_{001}) of a clay mineral because the stronger cation-water bonds reduce the cation's attraction to the clay surface. This stabilization of cations within the interlayer region by their surrounding water molecules results in increased spacing between the clay layers, leading to overall swelling.

5.3.2 Cation Type and Hydration-Dependent Swelling Mechanisms of Homoionic Saturated Montmorillonite at $\xi = 0.250$

This section analyses how variations in interlayer cation type affect the hydration structure and basal spacing (d_{001}) of montmorillonite at a layer charge of $\xi = 0.250$. At $\xi = 0.250$, the d_{001} value (which ranges from 12.18 to 12.65 Å) increases as cation diameter increases ($K^+ > Ca^{2+} > Na^+ > Mg^{2+}$) when 8 water molecules form a single, in-plane layer around each cation. This arrangement results in a monohydrate formation (1W), as evidenced by the d_{001} values falling within the typical range for a single layer of water. The expansion behaviour varies slightly depending on the type and valence of the interlayer cation: Na^+ -montmorillonite (Figure 5.1; top-left) shows the largest basal spacing at each hydration level among the monovalent systems. Sodium ions, with relatively small ionic radius and moderate hydration energy, allow more symmetric hydration shells and promote easier intercalation of water. This leads to a relatively open interlayer structure and higher swelling capacity. K^+ -montmorillonite (Figure 5.1; top-right) exhibits slightly smaller d_{001} values at equivalent hydration levels compared to Na^+ . Potassium ions have lower hydration energy and a larger ionic radius forming inner-sphere complexes that limit water penetration. As a result, K^+ -montmorillonite swells less,

consistent with its known non-swelling behaviour at high K^+ concentrations. Ca^{2+} -montmorillonite (Figure 5.1; down-left) shows a gradual increase in d_{001} with hydration, though the overall expansion is smaller than for Na^+ . The divalent Ca^{2+} cations possess higher charge density and stronger electrostatic attraction to the negatively charged clay layers, forming tightly bound hydration shells that resist interlayer expansion. Mg^{2+} -montmorillonite (Figure 5.1; down-right) exhibits the least expansion among all systems. Mg^{2+} ions have the highest hydration energy and smallest ionic radius, causing water molecules to bind very strongly in the first hydration shell. This strong coordination limits further water insertion into the interlayer, resulting in smaller basal spacing increases and more stable hydrated structures.

The comparison between *trans-vacant* (*tv*) and *cis-vacant* (*cv*) layer configurations shows only minor differences in d_{001} spacing. The curves nearly overlap, indicating that the layer vacancy distribution exerts limited influence on the swelling behaviour at this charge density ($\xi = 0.250$). Slightly higher basal spacings for *cv* configurations at higher hydration levels may result from subtle structural relaxation that facilitates more symmetric hydration around interlayer cations.

In the case of divalent cations (Ca^{2+} and Mg^{2+}), the smaller increase in d_{001} with hydration correlates with the stronger electrostatic binding between the cations and the clay layers, and the formation of inner-sphere complexes, as seen in molecular simulations. Conversely, Na^+ and K^+ exchange forms display weaker interlayer binding and greater flexibility, allowing easier expansion. These differences explain why Na^+ -montmorillonite typically exhibits the highest swelling capacity, while K^+ and Mg^{2+} -montmorillonites are more stable and less expandable. The results also indicate that cation valence and hydration energy jointly determine the interlayer structure and swelling response.

At low hydration levels (1–2 H_2O per cation), water–clay interactions dominate. The first few water molecules are directly coordinated to the exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and to the negatively charged oxygen atoms of the tetrahedral silicate surface. This gives rise to inner-sphere hydration complexes, where the cations are located close to the basal surface, and the water dipoles are oriented toward the clay layer. The strong electrostatic attraction between the cations and the basal oxygen atoms stabilizes this configuration and limits layer expansion. As additional water molecules enter the interlayer (≥ 4 H_2O per cation), water–water interactions become increasingly significant. The newly introduced molecules tend to form hydrogen bonds with the water molecules already bound to the cations, leading to the growth of outer-sphere hydration shells. These layers are less constrained by the clay surface and exhibit more fluid-like characteristics, allowing partial rearrangement of the hydrogen-bond network. The onset of these water–water interactions correspond to the observed increase in d_{001} , marking the transition from a tightly bound single hydration layer to a more open, structured configuration.

The arrangement of interlayer water depends strongly on the type of exchangeable cation. In Na^+ -montmorillonite, the cations typically reside near the midplane of the interlayer at moderate hydration, surrounded by a nearly symmetric first hydration shell. This geometry allows the development of an ordered two-dimensional hydrogen-bonded water layer parallel to the clay surface. The formation of this structured water network results in an observable stepwise increase of d_{001} spacing up to ~ 12.5 – 13 Å. For Ca^{2+} and Mg^{2+} -montmorillonite, the strong electrostatic attraction between the divalent cations and the silicate layers restricts their mobility and confines water molecules in compact hydration shells. The result is a more rigid interlayer structure, with limited

hydrogen-bond connectivity across adjacent water molecules. This explains the smaller d_{001} expansion and the reduced degree of swelling. In contrast, K^+ -montmorillonite shows weak water–clay and water–water interactions because K^+ ions tend to remain in inner-sphere complexes close to the clay surface, and the hydration shell is incomplete. Consequently, fewer water molecules can bridge between adjacent cations or surfaces, leading to minimal layer expansion.

The balance between water–clay and water–water forces ultimately control the stability and reversibility of the swelling process. When water–clay attraction is strong (as in Mg^{2+} and Ca^{2+} -montmorillonite), the hydrogen-bond network remains localized and stable, producing limited swelling but high structural rigidity. When water–water interactions dominate (as in Na^+ -montmorillonite), the network becomes more extended and dynamic, promoting higher swelling but also greater reversibility during dehydration.

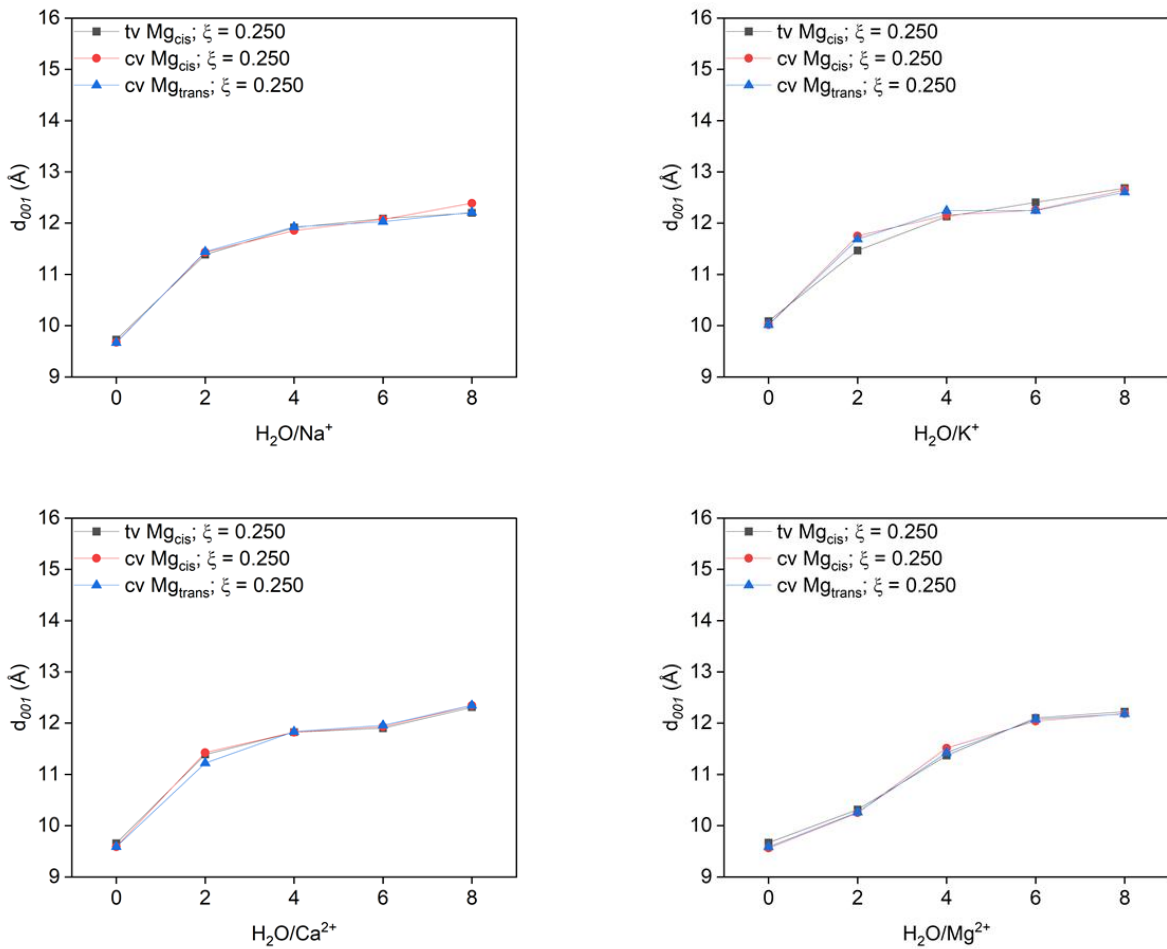


Figure 5.1: d_{001} as function of $H_2O/cation$ with $\xi = 0.250$

5.3.3 Cation Type and Hydration-Dependent Swelling Mechanisms of Homoionic Montmorillonite at $\xi = 0.500$

The swelling behaviour of montmorillonite at $\xi = 0.500$ is analysed to determine how cation type and hydration interactions govern changes in d_{001} and interlayer structure. For $\xi = 0.500$, the significant increase in d_{001} spacing is a result of a combination of factors. While the cations play a role in maintaining charge balance, the presence of water molecules and their hydration of these cations are critical in determining the extent of the d_{001} increase. The size of the cation alone does not fully dictate this expansion because the water-mediated interaction is a dominant factor in swelling. Ca^{2+} and Mg^{2+} cations induce a single layer of water molecules within the clay structure, resulting in a d_{001} of 12.07-12.20 Å, whereas Na^+ and K^+ cations lead to a larger spacing of 14.87-14.99 Å, characteristic of a bi-hydrated formation (2W). montmorillonite swells from dry state to highly hydrated states, water in the interlayer will form integer-layer arrangements. For Na^+ -hydrated montmorillonite, the basal spacing increases sharply from approximately 9.8 Å in the dehydrated state to about 15 Å at the highest hydration level (8 $\text{H}_2\text{O}/\text{Na}^+$). This substantial expansion indicates a strong hydration capacity of Na^+ ions, which readily attract and accommodate multiple layers of water molecules in the interlayer region. The progressive increase in d_{001} consistent with the well-documented swelling behaviour of Na-montmorillonite. The three model configurations (*tv* Mg_{cis} , *cv* Mg_{cis} , and *cv* Mg_{trans}) yield nearly identical results, implying that structural variations have a negligible effect compared with the dominant role of Na^+ hydration.

The K^+ -hydrated montmorillonite exhibits a trend similar to Na^+ , with d_{001} increasing from approximately 9.8 Å to nearly 15 Å as hydration progresses. However, the overall swelling is slightly less pronounced. This behaviour arises from the lower hydration energy and larger ionic radius of K^+ , which lead to weaker hydration forces and a reduced ability to expand the interlayer. K^+ tends to reside closer to the basal surface, maintaining partial dehydration and thereby constraining interlayer expansion compared to Na^+ . As in the Na^+ -montmorillonite, the three structural models produce nearly overlapping results, indicating that the hydration process governs swelling more strongly than the initial structural orientation.

In the Ca^{2+} -hydrated montmorillonite, the d_{001} increases from approximately 9.8 Å to around 12 Å at low water content and then stabilizes with further hydration. This indicates the formation of a stable double-layer hydrate that persists throughout the studied hydration range. The limited expansion results from the strong electrostatic attraction between the divalent Ca^{2+} ions and the negatively charged clay layers. Each Ca^{2+} ion forms a compact hydration shell that restricts the entry of additional water molecules. Consequently, the interlayer space remains stable at approximately 12 Å. The negligible differences among the three model configurations again highlight that the swelling behaviour is primarily controlled by cation-clay and cation-water interactions rather than by layer orientation or stacking variations.

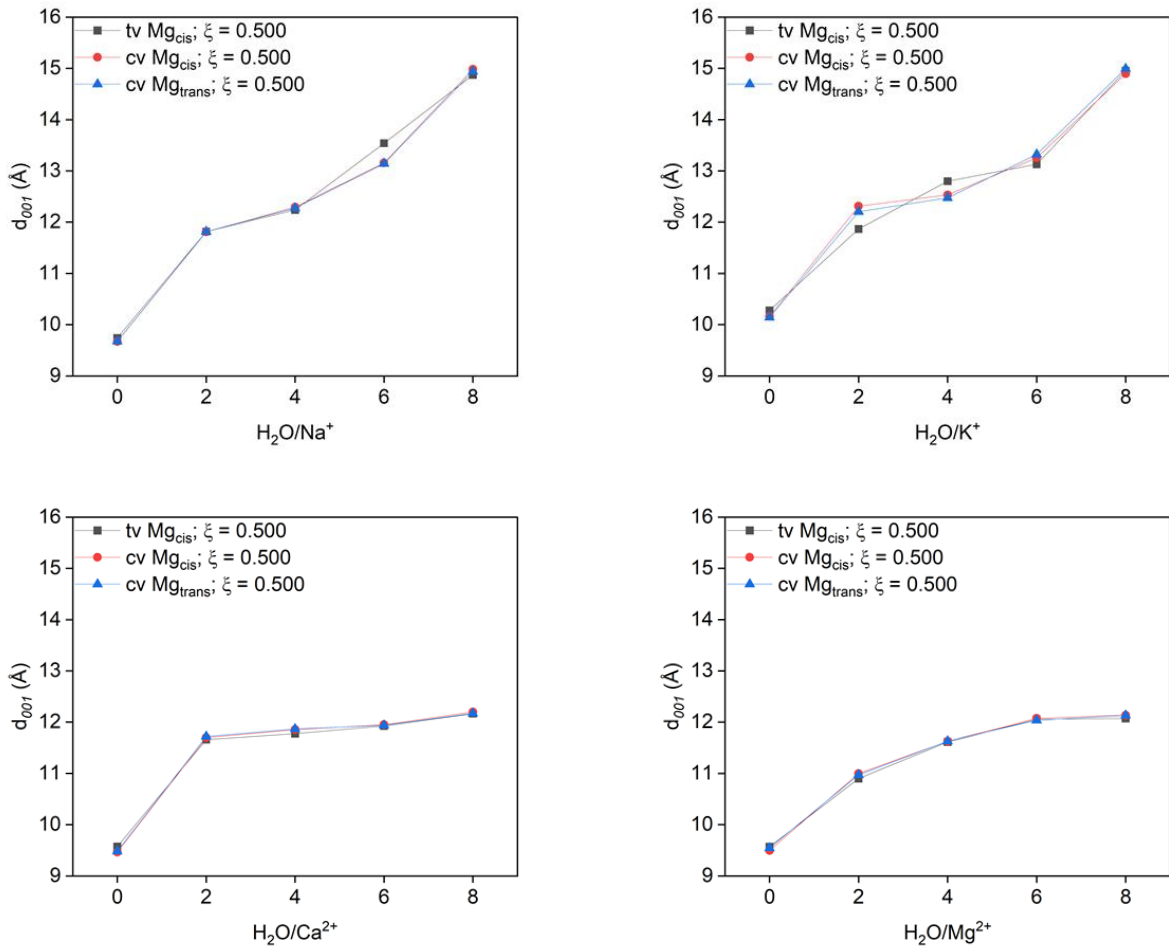
The Mg^{2+} -hydrated montmorillonite shows the least degree of swelling among all the examined cations. The d_{001} increases slightly from about 9.8 Å to nearly 12 Å and then plateaus, indicating the formation of a stable double layer hydration state. Mg^{2+} , possessing the highest charge density and strongest hydration energy, forms a rigid and stable hydration shell that tightly binds to both the clay surface and water molecules. This strong electrostatic interaction restricts further expansion of the interlayer and prevents the formation of higher-order hydration states. The near-identical curves for

$tv\text{ Mg}_{cis}$, $cv\text{ Mg}_{cis}$, and $cv\text{ Mg}_{trans}$ confirm that the dominant factor controlling swelling is the hydration energetics of Mg^{2+} rather than structural configuration.

Monovalent cations (Na^+ and K^+) exhibit substantial expansion with increasing hydration, whereas divalent cations (Ca^{2+} and Mg^{2+}) show restricted swelling and early stabilization. The differences in swelling behaviour can be attributed to the combined effects of ionic charge density, electrostatic attraction, and hydration energy. Monovalent cations, with lower charge density, interact weakly with the clay surfaces, allowing greater interlayer flexibility and easier incorporation of water molecules. In contrast, divalent cations form stronger electrostatic bonds with the negatively charged clay layers, resulting in compact and stable hydration shells that resist further swelling. Among the divalent cations, Mg^{2+} exhibits the smallest expansion due to its smaller ionic radius and higher hydration energy, which lead to a more rigid and tightly bound hydration structure.

The correlation between d_{001} and the hydration state of interlayer cations highlights the interplay between electrostatic forces and hydration thermodynamics. In systems with monovalent cations (Na^+ and K^+), weaker electrostatic attraction allows the incorporation of multiple water layers, promoting stepwise swelling transitions. Conversely, divalent systems (Ca^{2+} and Mg^{2+}) exhibit stronger cation–surface binding and compact hydration, limiting interlayer expansion to a stable double-layer configuration.

The difference in the number of unit cells used for modelling reflects the distinct electrostatic environments associated with each cation type. For Na^+ and K^+ -hydrated montmorillonite, 2UC adequately capture the relatively homogeneous swelling behaviour, as monovalent ions interact weaker with the clay surfaces, leading to a more uniform hydration structure. In contrast, 4UC cells are required for Ca^{2+} and Mg^{2+} systems to account for their stronger electrostatic interactions and localized charge compensation effects. The larger simulation domain ensures that the anisotropy and heterogeneity of divalent cation hydration environments are realistically represented. A clear trend in swelling capacity is observed among the different cations: $\text{Na}^+ \approx \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. This sequence highlights the key role of ionic charge and hydration energy in controlling interlayer expansion. Monovalent cations, with lower charge densities, allow more extensive water penetration and layer separation, while divalent cations maintain tighter interlayer cohesion through stronger Coulombic binding and specific ion-surface interactions. The effect of increasing layer charge amplifies this behaviour for monovalent systems but has limited influence in divalent systems.

Figure 5.2: d_{001} as function of $H_2O/cation$ with $\xi = 0.500$

5.3.4 Structural Configuration of Monohydrated and Bihydrated Montmorillonite at Different Layer Charges ($\xi = 0.250$ and $\xi = 0.500$)

This section illustrates the structural configurations of hydrated montmorillonite with different interlayer cations, highlighting the transition from monohydrated (1W) to bihydrated (2W) states as a function of layer charge and cation type. Figures 5.3, 5.4, 5.5, and 5.6 show the structure of $cv Mg_{cis}$ Na^+ , K^+ , Ca^{2+} , and Mg^{2+} -hydrated montmorillonite. At $\xi = 0.250$ as mentioned above, the formation of water molecules forms a monohydrate (1W). The monohydrated 1W state of montmorillonite (MMT) hydration represents a specific structural change where a single plane of water molecules is incorporated into the interlayer space between the 2:1 clay layer. This results in a defined, single-layer hydration structure, causing a specific increase in the d_{001} (e.g., around 11.6-12.9 Å) due to the electrostatic attraction between the hydrated cations and the negatively charged clay sheets. In this state, the water molecules and cations are organized in a distinct structural arrangement, but this arrangement can be heterogeneous. Water molecules first adsorb to the external surface of the clay and then diffuse into the interlayer spaces. The hydrated cations within the interlayers attract water molecules, forming ordered arrangements around them. As water activity increases, water molecules are incorporated in discrete planes between the clay layers, leading to stepwise swelling. a single layer of water molecules occupies the interlayer space between the clay's silica sheets, with interlayer

cations like Na^+ being coordinated to the basal oxygen atoms and to several water molecules, typically forming an orthogonal coordination sphere. the 1W monohydrated structure represents a crucial low-hydration state where the interlayer space is occupied by a single layer of water molecules, interacting with and coordinating to the interlayer cations and the surrounding clay structure.

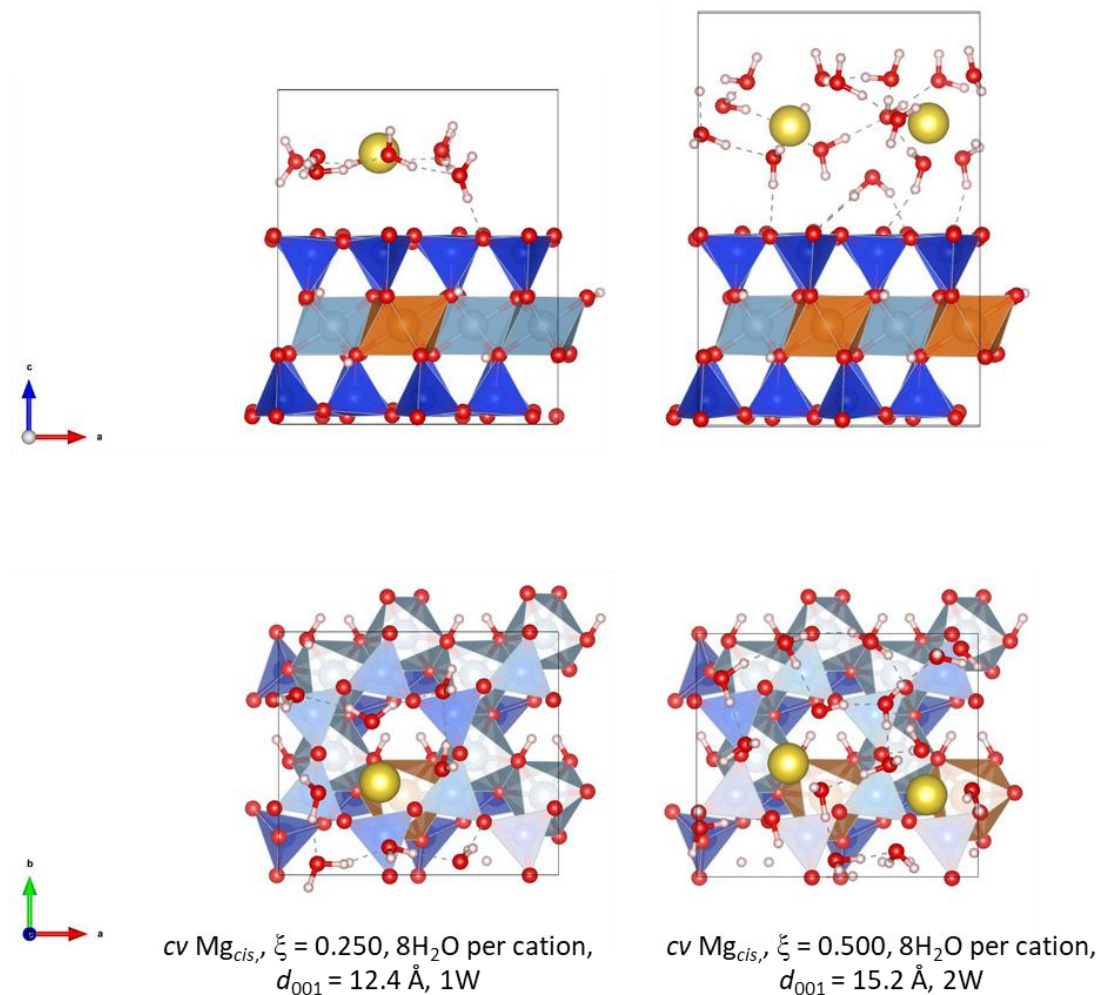


Figure 5.3: Structure of Na^+ -hydrated montmorillonite

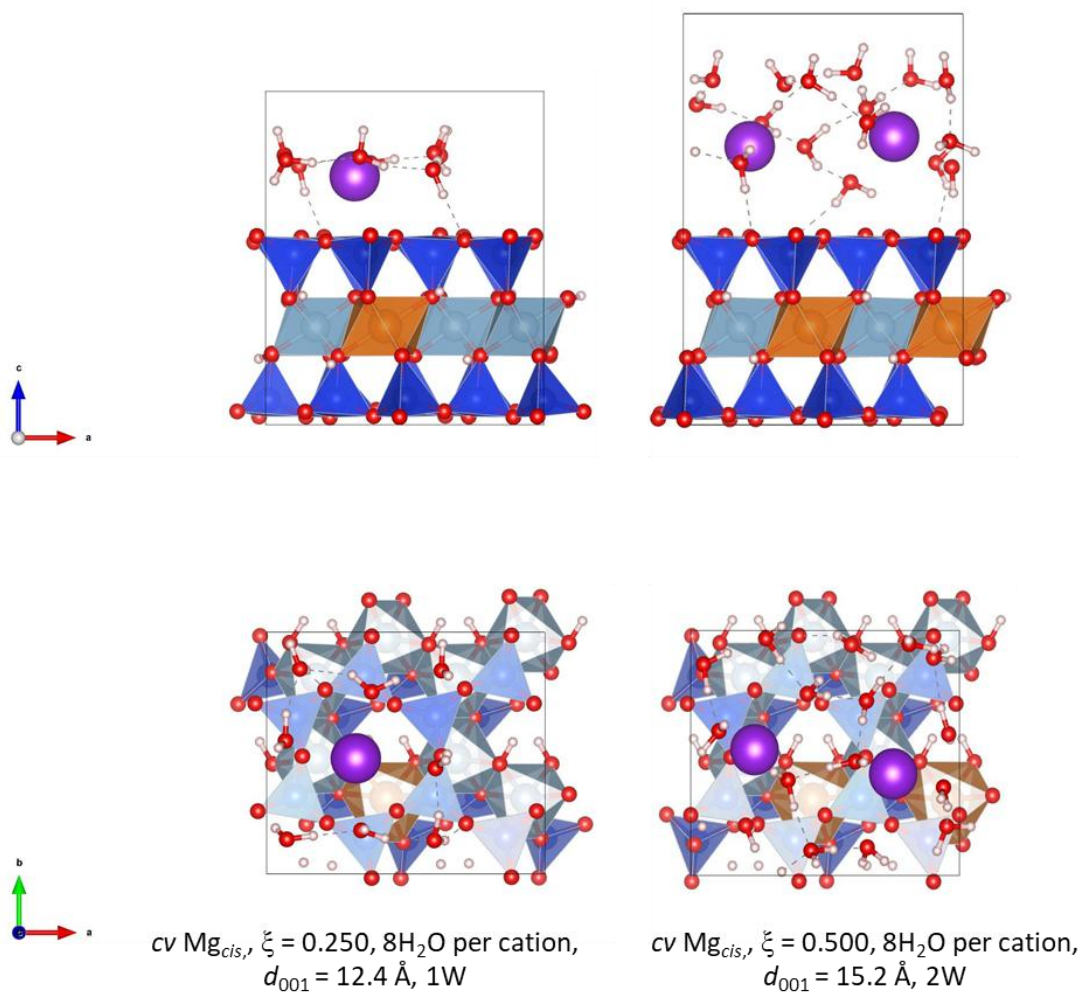


Figure 5.4: Structure of K^+ -hydrated montmorillonite

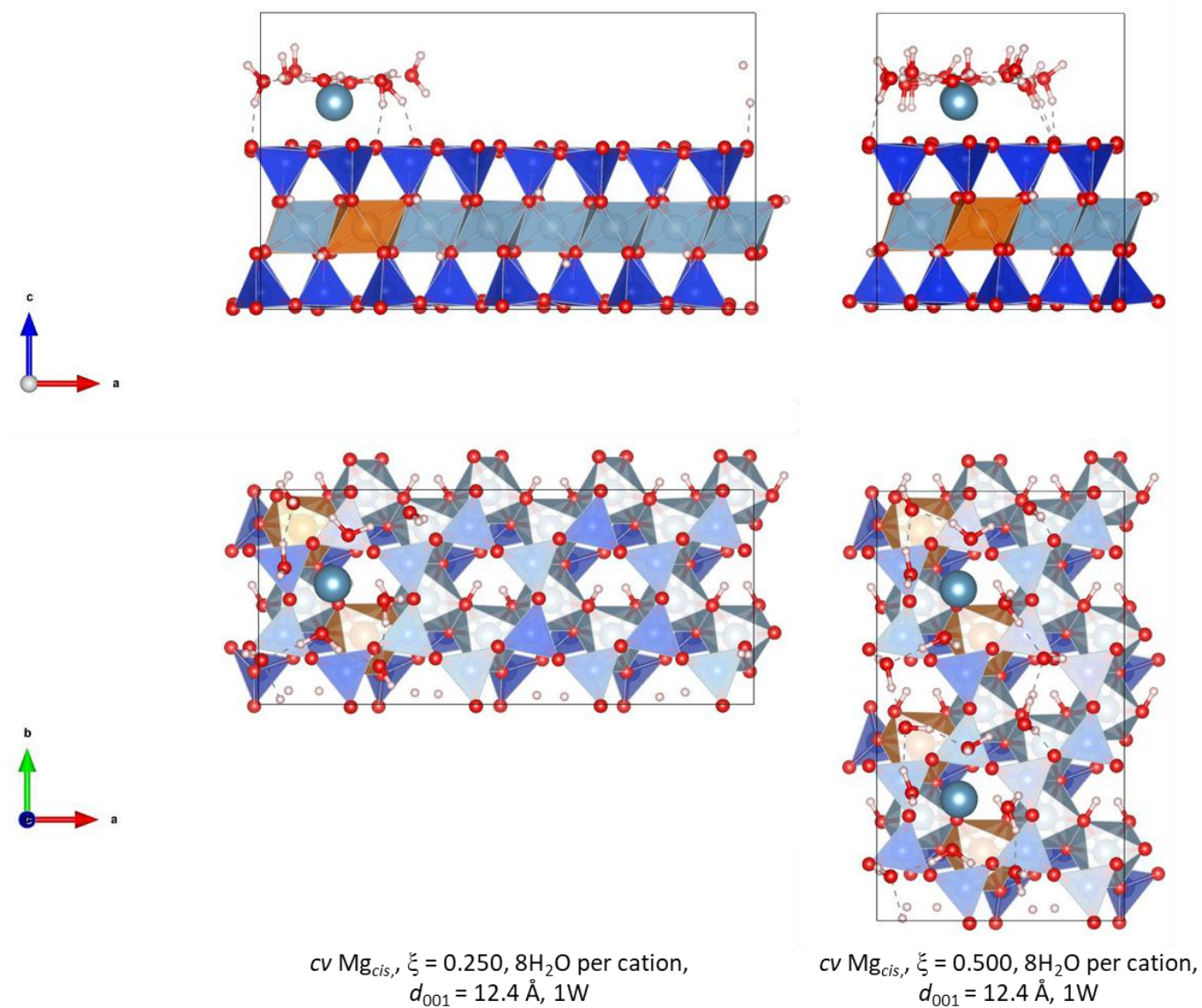
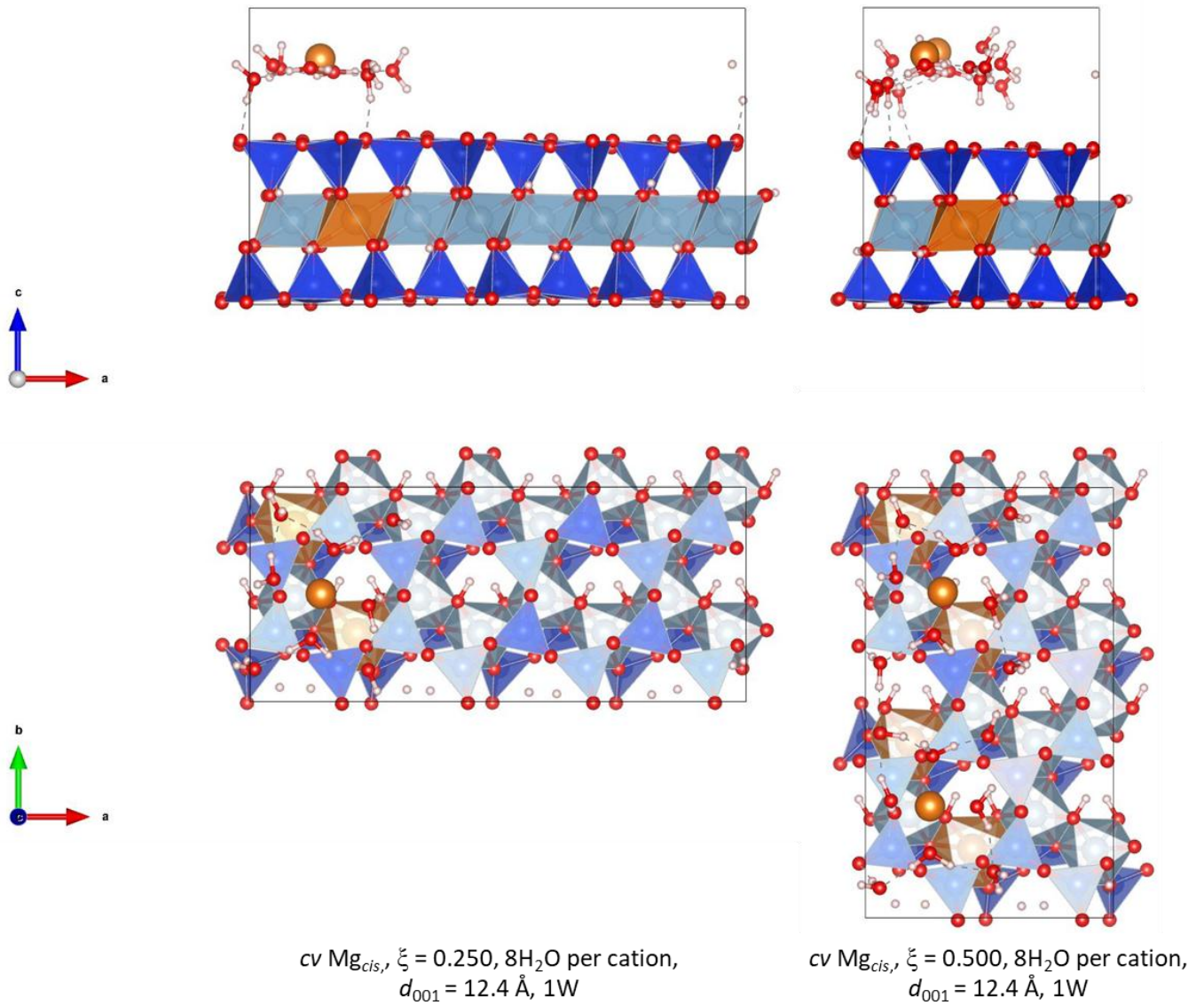


Figure 5.5: Structure of Ca^{2+} -hydrated montmorillonite

Figure 5.6: Structure of Mg^{2+} -hydrated montmorillonite

At $\xi = 0.250$, an increase in the number of water molecules causes swelling, which is indicated by an increase in the d_{001} value. However, the results obtained show that when the number of water molecules reaches 8 per cation, there is no longer a significant increase in the d_{001} value. This is because under these conditions, the interlayer space is still empty and free to be filled by water molecules without causing a significant increase in the d_{001} value.

At $\xi = 0.500$, the formation of water molecules differs between monovalent and divalent cations. For divalent cations, the formation of water molecules forms a monohydrate that is not much different from $\xi = 0.250$. However, for monovalent cations, the addition of 8 water molecules per cation causes the formation of a 2W. 2W montmorillonite is a hydrated state of montmorillonite clay where the interlayer space contains two layers of water molecules, leading to an expanded basal spacing compared to 0W or 1W states. Where 2W formation is a structural arrangement where two distinct layers of water molecules are intercalated within the interlayer space between the clay's structural layers, which consist of tetrahedral silica sheets and an octahedral aluminium sheet. This 2W state

represents a step in the stepwise hydration of montmorillonite, where water molecules form coordination shells around the interlayer cations and create a larger interlayer spacing, leading to swelling. The specific thickness and arrangement of these water layers depend on the interlayer cation's hydration energy, the overall layer charge of the montmorillonite. The formation of the 2W begins when six water molecules are added. At the 0.500 charge layer, these six water molecules enable the formation of a structure in which water molecules are arranged in octahedral coordination around the hydrated cation in the interlayer space, with approximately three water molecules interacting with the upper montmorillonite layer and three with the lower layer. This arrangement involves cationic interlayer water that is directly bound to the cation and surface water that is strongly hydrogen-bonded.

A one-layer water arrangement around a cation involves 3-4 water molecules, whereas a two-layer arrangement features six water molecules in an octahedral formation. For clay minerals in which water molecules are in excess of the two-layer arrangement (estimating a maximum of eight water molecules per cation), the water is oriented randomly similar to bulk water. We refer to this as a “three-layer” configuration.

5.4 Summary, Conclusion and Future Outlook

5.4.1 Summary

Density Functional Theory (DFT) simulations reveal that montmorillonite hydration and swelling occur in discrete steps governed by cation type, charge, and hydration energy. The d_{001} increases as water molecules enter the interlayer, forming hydration shells around cations that weaken electrostatic attraction to the clay surface. Monovalent cations (Na^+ , K^+) allow greater interlayer expansion due to weaker electrostatic binding, while divalent cations (Ca^{2+} , Mg^{2+}) produce tighter, more stable structures with limited swelling. Na^+ -hydrated montmorillonite exhibits the largest swelling capacity, followed by K^+ , Ca^{2+} , and Mg^{2+} .

At a lower layer charge ($\xi = 0.250$), all systems form a monohydrated (1W) structure, whereas at higher charge ($\xi = 0.500$), Na^+ and K^+ systems develop a bihydrated (2W) state. The hydration process transitions from direct cation-surface interactions at low water content to water-water hydrogen bonding at higher hydration, which drives stepwise expansion.

5.4.2 Conclusion

DFT modelling confirms that montmorillonite swelling is primarily controlled by the interplay between cation valence, hydration energy, and water content. Monovalent cations promote greater swelling through weaker cation-surface attraction and more extensive hydration, while divalent cations constrain expansion through strong electrostatic binding. Increasing water content transforms tightly bound monolayer states into more open bilayer configurations, stabilizing hydrated cations and increasing d_{001} spacing. The overall swelling trend follows $\text{Na}^+ \approx \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, highlighting the critical role of hydration thermodynamics and electrostatics in smectite swelling behaviour.

5.4.3 Future Outlook

The present DFT analysis provides valuable insight into the atomic-scale mechanisms governing montmorillonite hydration and swelling, yet several avenues remain open for advancing understanding and broadening applicability:

1. **Dynamic Hydration Mechanisms.** Future work should extend beyond static DFT models to ab initio molecular dynamics or reactive MD simulations to capture the time-dependent evolution of hydration shells, interlayer water exchange, and swelling pressure under varying temperature and pressure. Such approaches could clarify the kinetics and reversibility of the monolayer-to-bilayer transition.
2. **Influence of Mixed Cations and Natural Heterogeneity.** Since natural clays often contain mixed interlayer cations, future studies should explore competitive hydration and swelling behaviour in mixed-cation montmorillonites (e.g., $\text{Na}^+/\text{Ca}^{2+}$ systems). This would yield more realistic predictions for environmental and geotechnical contexts, including ion exchange and contaminant migration.
3. **Hydration Under Confinement and External Stress.** Coupling DFT with mechanical deformation or confining pressure models can help elucidate how stress, compaction, or burial depth affects swelling limits and hydration stability—key factors for applications in waste repository liners, shale gas extraction, and soil mechanics.
4. **Thermodynamic and Kinetic Modelling.** Future work could integrate free-energy calculations and potential force analyses to quantify the energetics of water intercalation and cation mobility, linking atomic-scale results with macroscopic swelling pressures observed experimentally.
5. **Environmental and Materials Applications.** The mechanistic insights from this study can guide the design of engineered clays with tailored swelling capacity for use in barrier materials, drug delivery, and ion-selective membranes. Controlled hydration could be exploited to tune permeability, ion exchange capacity, and structural resilience.
6. **Data-Driven and Machine Learning Approaches.** Combining DFT datasets with machine learning models could enable rapid prediction of swelling behaviour across diverse cation types, hydration states, and layer charges, reducing computational cost and accelerating materials screening for industrial applications.

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6 Adsorption, Desorption and Hydration Homoionic Saturated Montmorillonite in Different Relative Humidity

6.1 Introduction

Montmorillonite is well known for its remarkable ability to absorb and retain large quantities of water within its crystal structure. The degree of hydration, or the number of molecular water layers present between clay layers, varies with the surrounding relative humidity (r.h.), pressure, temperature, and type of interlayer cation (Mooney et al., 1952). Structurally, montmorillonite is a 2:1 phyllosilicate consisting of an alumina octahedral sheet sandwiched between two silica tetrahedral sheets. The weak van der Waals forces between these layers permit the ingress of water molecules, which organize into discrete monolayer, bilayer, or multilayer arrangements depending on environmental conditions.

The type of exchangeable cation occupying the interlayer sites (e.g., Na^+ , K^+ , Ca^{2+} , Mg^{2+}) plays a critical role in determining the hydration behaviour and interlayer spacing of montmorillonite. Cations with higher hydration energy, such as Na^+ , tend to promote greater water uptake and swelling, whereas cations like K^+ , with lower hydration energy, lead to more compact structures with reduced expansion (Norrish, 1954; Sposito and Prost, 1982; Berend et al., 1995; Laird, 1996). These variations in hydration behavior are directly related to the electrostatic balance within the interlayer region and influence the stability of the different hydration states (1W, 2W, or 3W).

Hydration state of montmorillonite changes with effective pressure and temperature. Increased pressure generally reduces hydration by forcing water out of the structure, while increasing temperature typically decreases hydration, although complex interactions with ions and water properties can occur, sometimes even increasing hydration if ice forms or for specific cation types and conditions. The hydration state of montmorillonite changes also with effective pressure and temperature (Bird 1984; Colten-Bradley 1987), meaning it is important to understand how hydration state influences the frictional strength of montmorillonite with depth. The relationship between temperature and hydration is not always simple. The type of interlayer cation, such as Na^+ , K^+ , or Ca^{2+} , can significantly influence how temperature affects hydration. Temperature also influences the properties of the pore water itself, further complicating the hydration response. Elevated temperatures, particularly in geological disposal scenarios, can lead to a reduction in swelling pressure, partly due to water loss and reduced double-layer forces (Yang, et al., 2021).

The interlayer cation type not only governs hydration but also directly influences the mechanical and frictional properties of montmorillonite. Experimental studies (Behnsen and Faulkner, 2013; Wang et al., 2025) have demonstrated that K^+ -saturated montmorillonite exhibits higher frictional strength than Na^+ -, Ca^{2+} -, or Mg^{2+} -montmorillonite under comparable hydration conditions. This difference arises from variations in cation hydration ability, water adsorption behaviour, and interlayer structural arrangement. The friction angle of montmorillonite decreases progressively with increasing water content, highlighting the direct relationship between hydration state, interlayer viscosity, and mechanical behaviour (Ying et al., 2024).

At the microscopic level, interlayer water molecules can adopt various structural configurations depending on cation coordination and charge distribution. XRD analyses reveal that interlayer water can exist in mono-, bi-, or tri-hydrated states, although the reflections often appear broad and asymmetric due to particle size effects, stacking disorder, and inhomogeneous layer charge (Watanabe and Sato, 1988; Sato et al., 1992). These structural variations strongly influence the swelling, rheology, and frictional properties of montmorillonite-rich materials.

The present study aims to investigate the interaction between water and two montmorillonite samples, Calcigel and Secursol UHP, under varying relative humidity at a constant temperature (20 °C). Additionally, this work examines the hydration behaviour of homoionic saturated montmorillonites (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) to understand how cation type and cation exchange capacity affect the extent of water absorption, interlayer expansion, and structural stability. The results are expected to provide valuable insights into the hydration mechanisms governing the physical and mechanical properties of homoionic saturated montmorillonite under environmental and geotechnical conditions.

6.2 Methods

The detailed of preparation of homoionic exchange samples follows the methodology described in the study by Steudel and Emmerich (2013) as described in section 2.2.

6.2.1 Materials

The materials characteristics of Calcigel and Secursol UHP were used in this study are describes in section 2.2.1.

6.2.2 Chemicals

The chemicals used in this study was listed in section 2.2.2.

6.2.3 Equipment

The equipments used in this study was listed in section 2.2.3.

6.2.4 Homoionic Saturated Sample Preparation

Homoionic saturated sample are prepared as mentioned section 2.2.4.; 2.2.5.; 2.2.6.; 2.2.7. and 2.2.8.

6.2.5 Adsorption, Desorption and Hydration of Smectite

Adsorption and hydration of Homoionic saturated sample methods included Relative Humidity Sample Preparation and water adsorption are mentioned in section 2.3.

6.3 Results and Discussion

6.3.1 Fraction of Homoionic Saturated Montmorillonite

This section describes the outcomes of the homoionic saturated montmorillonite preparation process, focusing on the particle size distribution and mass loss of Calcigel and Secursol UHP. The analysis highlights the proportion of ($<2\ \mu\text{m}$ and $>2\ \mu\text{m}$ fractions obtained after cation exchange and washing treatments. Differences between the two clay types, as well as the effects of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} saturation on dispersion, hydration, and structural stability, are examined to understand their influence on clay reactivity and purity.

Figure 6.1 shows the fractions produced in the homoionic sample preparation process. The fraction $<2\ \mu\text{m}$ produced is at least 57% of the mass of the initial raw material sample. This fraction is rich in fine-grained clay minerals, which are the main components responsible for soil plasticity and water retention capacity. The fraction $>2\ \mu\text{m}$ ranges from 28–33%.

Calcigel exhibit a greater proportion of fine particles ($< 2\ \mu\text{m}$), ranging from 58–65%, compared with 56–57% in the Secursol UHP. Conversely, Secursol UHP contain a slightly higher proportion of coarse particles ($>2\ \mu\text{m}$), approximately 31–33%, relative to 28–29% in Calcigel. The overall weight loss during homoionic treatment is consistently higher in Calcigel (6–14%) than in Secursol UHP (8–13%). Among these, Cal_Na exhibits the greatest mass loss (14%), while Cal_Ca shows the lowest (6%).

Calcigel possesses a finer texture and greater dispersibility than Secursol UHP. The finer grain size may be attributed to the higher proportion of expandable smectitic layers and fewer non-swelling impurities in Calcigel. The higher mass loss in Calcigel also suggests greater removal of soluble materials and better cation exchange efficiency, consistent with its higher cation exchange capacity and structural openness. The coarser particle size and lower weight loss of Secursol UHP imply the presence of aggregated structures and more resistant impurities, possibly due to differences in initial mineralogy or stronger interparticle bonding. These characteristics reduce the efficiency of dispersion and ion exchange during the homoionic exchange preparation. The type of exchangeable cation strongly influences both particle size distribution and weight loss. For both clay types, the Na^+ and K^+ forms tend to exhibit higher weight loss (13–14%) than the Ca^{2+} and Mg^{2+} forms (6–10%). This behaviour can be related to the hydration energy and ionic mobility of the cations. Monovalent cations (Na^+ and K^+) are more mobile and can exchange more readily with the natural interlayer cations, enhancing removal of soluble salts and weakly bound materials during washing. Consequently, these treatments result in higher mass losses and slightly greater dispersion. On the other hand, divalent cations (Ca^{2+} and Mg^{2+}) form stronger electrostatic bonds with the clay surface and promote flocculation rather than dispersion. Their smaller hydration radii and higher charge density contribute to interlayer contraction and aggregation, thereby reducing weight loss but favouring a more stable particle structure.

Calcigel demonstrates higher reactivity and finer dispersion compared to Secursol UHP, indicating more expandable layers and fewer structural impurities. Na^+ and K^+ promote greater mass loss and dispersion due to their higher hydration and exchange mobility, while Ca^{2+} and Mg^{2+} enhance structural cohesion and reduce particle loss.

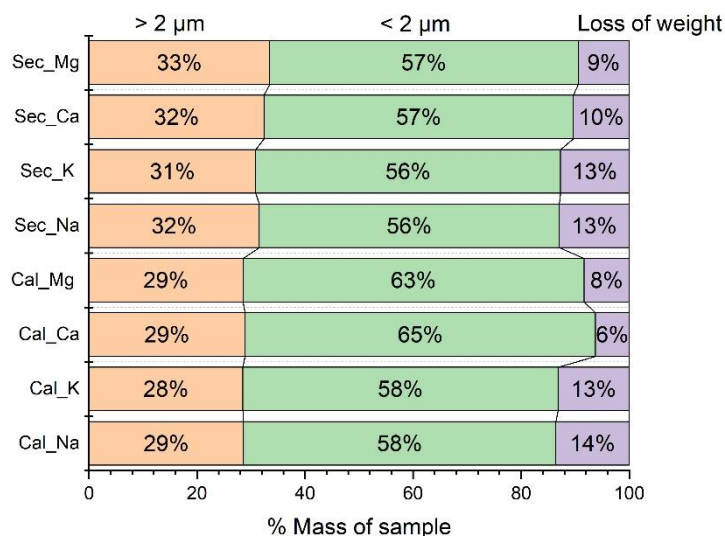


Figure 6.1: % Mass of sample

6.3.2 Dialysis Process

Dialysis measurement of homoionic saturation montmorillonite involve using dialysis membrane tubes to remove soluble salts and control cation exchange. Figures 6.2 present the electrical conductivity ($\mu\text{S}/\text{cm}$) as a function of dialysis time (hours) for two montmorillonite sources, Calcigel and Secursol UHP, each saturated with various exchangeable cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). The conductivity behaviour reflects the removal of soluble ions, the degree of cation exchange, and the effectiveness of the dialysis process in producing pure homoionic saturated montmorillonite.

In both figures (Calcigel; left and Secursol UHP; right) conductivity starts very high at the beginning of dialysis and decreases sharply over time, eventually stabilizing at a low constant value. At the beginning of the Calcigel samples dialysis process (0–70 hours), all samples exhibited a pronounced increase in conductivity, which then rapidly decreased with time. The Na^+ -homoionic saturated montmorillonite (Cal_Na) displayed the highest initial conductivity, reaching approximately 550 $\mu\text{S}/\text{cm}$, followed by K^+ -homoionic saturated montmorillonite Calcigel (Cal_K) with a peak around 450 $\mu\text{S}/\text{cm}$. In contrast, Ca^{2+} - and Mg^{2+} -homoionic saturated montmorillonite (Cal_Ca and Cal_Mg) showed much lower initial conductivity values, around 40–50 $\mu\text{S}/\text{cm}$. After approximately 100 hours, the conductivity of all systems declined sharply and stabilized near 20 $\mu\text{S}/\text{cm}$, remaining nearly constant beyond 150 hours. In Secursol UHP, all samples exhibit a sharp rise in conductivity, which corresponds to the release of soluble salts and loosely bound exchangeable ions from the clay suspension into the surrounding water at the beginning of dialysis (0–50 hours). Among the tested samples, Na^+ -homoionic saturated montmorillonite (Sec_Na) shows the highest peak conductivity (≈ 320 $\mu\text{S}/\text{cm}$), followed by K^+ -homoionic saturated montmorillonite (Sec_K) (~ 140 $\mu\text{S}/\text{cm}$). In contrast, the Ca^{2+} (Sec_Ca) and Mg^{2+} (Sec_Mg) samples display much lower conductivity peaks (~ 30 – 40 $\mu\text{S}/\text{cm}$).

The Calcigel exhibit higher maximum conductivity values (up to ~ 560 $\mu\text{S}/\text{cm}$ for Na^+ and ~ 450 $\mu\text{S}/\text{cm}$ for K^+) than the Secursol (~ 320 $\mu\text{S}/\text{cm}$ for Na^+ and ~ 140 $\mu\text{S}/\text{cm}$ for K^+). This indicates that the Calcigel initially contains more soluble salts and exchangeable ions. The higher ionic content may be attributed to variations in the raw material composition, the initial saturation efficiency, or the presence of more soluble accessory minerals. In contrast, the Secursol UHP reach equilibrium more quickly and exhibit

lower overall conductivity, suggesting a higher initial purity and more efficient ion exchange during preparation.

Na⁺-homoionic saturated montmorillonite exhibits the highest conductivity due to the high ionic mobility and weak electrostatic binding of Na⁺ to the clay surface. K⁺-homoionic saturated montmorillonite shows moderately high conductivity, though lower than Na⁺, consistent with the larger ionic radius and lower hydration energy of K⁺, which limit its mobility. Ca²⁺ and Mg²⁺ samples show the lowest conductivity values, indicating that divalent cations are strongly bound to the negatively charged clay layers, leading to lower diffusivity and ion release during dialysis.

After approximately 100–150 hours, the conductivity of all samples stabilizes at a low and nearly constant value (~10–20 $\mu\text{S}/\text{cm}$), indicating that ionic equilibrium has been achieved and that further removal of exchangeable ions is negligible. Both Calcigel and Secursol UHP reach this equilibrium, though the Calcigel series requires slightly longer dialysis, reflecting a greater initial ionic load. The final equilibrium conductivity levels are comparable for both clay types, confirming that the dialysis process successfully produced fully purified homoionic saturated montmorillonite irrespective of the original raw material.

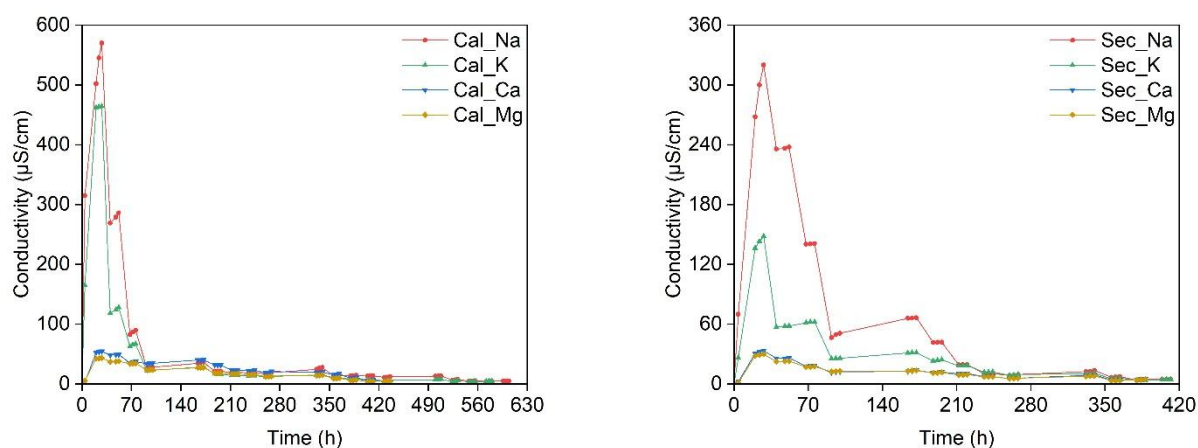


Figure 6.2: Conductivity as function of time dialysis measurement, Calcigel (left) and Secursol UHP (right)

6.3.3 CEC, Moisture, Exchangeable Cation and Degree of Homoionic Saturation

This section presents the CEC, minimum water content, exchangeable cation composition, and homoionic saturation degree of Calcigel and Secursol UHP. The analysis compares raw and homoionic saturated forms to evaluate the effects of cation type, particle size, and clay composition on ion-exchange efficiency and hydration behaviour. Table 6.2 displays the results of cation exchange capacity (CEC), moisture content ($w_{\min}$), exchangeable cations, and the degree of homoionic saturation for the Calcigel (Cal) and Secursol UHP (Sec) samples. Both raw and homoionic saturated forms were analysed to evaluate their cation-exchange performance, hydration characteristics, and the influence of particle size and cation type on the efficiency of ion substitution.

The Calcigel raw (Cal_R) and Secursol UHP Raw (Sec_R) samples exhibit CEC values of 61 and 87 $\text{cmol}(+)/\text{kg}$, respectively, indicating that Secursol UHP possesses a higher layer charge density and greater potential for cation exchange. Correspondingly, the Sec_R sample also displays a higher

minimum water content (14.83%) than Cal_R (10.19%), suggesting a stronger affinity for water due to a greater negative surface charge. Both raw samples are dominated by divalent cations, primarily Ca^{2+} , reflecting their natural state as Ca montmorillonite. The relatively high concentrations of these cations indicate that the montmorillonite interlayers are initially occupied by strongly bound divalent species, typical of natural bentonites. The higher CEC and water content of Sec_R imply that Secursol contains a more smectitic composition and fewer non-clay mineral impurities compared to Calcigel.

Homoionic exchange with sodium, a significant increase in Na^+ concentration is observed, especially in the $<2\ \mu\text{m}$ fraction. For example, the Na^+ content increases to 117.7 cmol(+)/kg in Cal_Na $<2\ \mu\text{m}$ and 161.2 cmol(+)/kg in Sec_Na $<2\ \mu\text{m}$, both corresponding to saturation degrees near 98%. This demonstrates that $<2\ \mu\text{m}$ fractions exhibit much higher ion-exchange efficiency than $>2\ \mu\text{m}$ particles. The enhanced exchange capacity of the $<2\ \mu\text{m}$ fraction arises from its higher surface area, larger number of exchange sites, and fewer structural impurities such as quartz, which are more common in $>2\ \mu\text{m}$ fractions. The minimum water content ($w_{\min}$) of Na^+ -homoionic saturated montmorillonite (Cal_Na = 7.78%; Sec_Na = 6.81%) is higher than that of Cal_Na $>2\ \mu\text{m}$ (1, 2, 3 and 4) and Cal_Na $>2\ \mu\text{m}$ (1, 2, 3 and 4). The higher hydration of Na^+ results from its relatively strong hydration shell and greater swelling ability.

The K^+ -homoionic saturated montmorillonite (Cal_K $<2\ \mu\text{m}$ and Sec_K $<2\ \mu\text{m}$) show slightly reduced CEC values (72 and 82 cmol(+)/kg, respectively) and lower $w_{\min}$ (5.08–5.67%) compared to their Na^+ -exchanged counterparts. Despite achieving a similar degree of homoionic saturation (96–97%), the K^+ -forms exhibit less swelling and water uptake. This behavior is attributed to the larger ionic radius and weaker hydration energy of K^+ , which promote a collapse of the interlayer space. K^+ tends to fit tightly into the hexagonal cavities of the silicate layers, reducing the number of accessible interlayer sites for water molecules and thereby lowering hydration and swelling potential.

Ca^{2+} and Mg^{2+} -homoionic saturated montmorillonite exhibit the highest CEC values and water contents among all treatments. In particular, Sec_Mg $<2\ \mu\text{m}$ and Sec_Ca $<2\ \mu\text{m}$ reach 105 and 104 cmol(+)/kg, respectively, while their $w_{\min}$ values exceed 12%. This behaviour reflects the strong hydration energy and high charge density of divalent cations, which promote strong electrostatic attraction to the negatively charged clay layers and facilitate the formation of multiple, ordered water layers in the interlayer space. However, the higher charge of Ca^{2+} and Mg^{2+} also leads to tighter interlayer binding, resulting in less interlayer expansion compared to Na^+ montmorillonite. This indicates that although divalent cations attract more bound water, they restrict the degree of swelling relative to monovalent cations.

A comparison between Calcigel and Secursol UHP reveals that Secursol UHP consistently exhibits higher CEC values, greater water retention, and slightly higher degrees of homoionic saturation across all cation types. Despite different exchange cations, both Calcigel and Secursol UHP maintain high degrees of homoionic saturation (~95–98%), indicating successful homoionic saturated processes.

Table 6.1: CEC, exchangeable cations of samples and degree of homoionic saturation

Sample	CEC	w_{min}	Exchangeable cations [cmol(+)/kg] ± 1						Degree of homoionic saturation (%)
	[cmol(+)/kg]	[%] ± 1 , 200 °C, 24h	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	Total	%CEC	
Cal_R	61	10.19	20.1	49.5	5.1	1.6	76	125	-
Cal_Na > 2 μ m (1)	23	2.29	0.0	0.6	35.6	0.5	37	160	-
Cal_Na > 2 μ m (2)	30	2.81	0.0	4.1	37.0	0.8	42	141	-
Cal_Na > 2 μ m (3)	20	2.55	0.0	2.8	23.0	0.6	26	130	-
Cal_Na > 2 μ m (4)	20	2.07	0.0	2.4	24.9	0.4	28	137	-
Cal_Na < 2 μ m	80	7.78	0.3	0.0	117.7	1.9	120	150	98
Cal_K < 2 μ m	72	5.08	0.3	0.0	4.2	111.8	116	162	96
Cal_Ca < 2 μ m	84	11.30	0.1	68.5	1.1	2.6	72	86	95
Cal_Mg < 2 μ m	86	12.25	70.8	0.2	1.0	2.8	75	87	95
Sec_R	87	14.83	16.1	50.7	3.8	1.3	72	83	-
Sec_Na > 2 μ m (1)	59	6.45	0.3	3.9	77.9	0.6	83	140	-
Sec_Na > 2 μ m (2)	63	7.32	0.3	7.6	82.9	1.0	92	145	-
Sec_Na > 2 μ m (3)	66	7.15	0.4	8.5	79.8	0.6	89	136	-
Sec_Na > 2 μ m (4)	69	7.45	0.3	7.6	94.8	0.8	104	151	-
Sec_Na < 2 μ m	99	6.81	0.4	2.2	161.2	1.5	165	166	98
Sec_K < 2 μ m	82	5.67	0.1	2.7	1.0	133.1	137	166	97
Sec_Ca < 2 μ m	104	12.54	0.6	85.8	1.0	2.3	90	86	96
Sec_Mg < 2 μ m	105	13.78	85.8	1.0	0.8	1.8	89	85	96

6.3.4 Water Content as Function of Relative Humidity

Figures 6.3 illustrate the relationship between water content (%) and relative humidity (r.h., %) for the montmorillonite samples Cal_R (Calcigel) and Sec_R (Secursol), each evaluated at different equilibration periods (initial, 24 hours, and 48 hours). The data reveal the progressive hydration response of homoionic saturated montmorillonite as a function of atmospheric humidity.

At low relative humidity (<20%), the water content remains minimal (approximately 3-6%), corresponding to surface adsorption on external surfaces and limited interlayer hydration (monolayer or “one-water-layer” state). As relative humidity increases between 40-75%, a gradual rise in water content is observed. This stage is attributed to multilayer adsorption and the progressive penetration of water molecules into interlayer galleries, resulting in partial swelling of the clay structure. At high humidity levels ($\geq 90\%$), both samples demonstrate a pronounced increase in water uptake. This rapid rise reflects interlayer expansion and possible capillary condensation, indicative of the transition toward a “two-water-layer” hydration state.

Sec_R montmorillonite consistently adsorbs more water than Cal_R across all humidity levels. At 95-100% r.h., Sec_R attains a maximum water content of approximately 27-28%, whereas Cal_R reaches only $\sim 22\%$. Sec_R possesses a higher CEC compared to Cal_R, enabling greater electrostatic attraction of water molecules to interlayer cations, thereby enhancing total hydration.

The measurements conducted after 24 hours and 48 hours show negligible differences, indicating that adsorption equilibrium is achieved within 24 hours for both samples. The water uptake curve at initial exposure is slightly lower, suggesting that hydration initially occurs on the outer surfaces, followed by a slower diffusion of water molecules into interlayer spaces until full equilibrium is attained. The near-identical results after 24 and 48 hours confirm that both Cal_R and Sec_R exhibit rapid and stable hydration dynamics under controlled humidity conditions.

The greater water adsorption of Sec_R highlights its stronger affinity for moisture, likely governed by the nature of its exchangeable cations (such as Na^+ and Ca^{2+}). These cations have higher hydration energies and facilitate water molecule coordination within the interlayer, resulting in more significant swelling. In contrast, the relatively lower hydration of Cal_R suggests the presence of cations with weaker hydration shells or structural features limiting expansion.

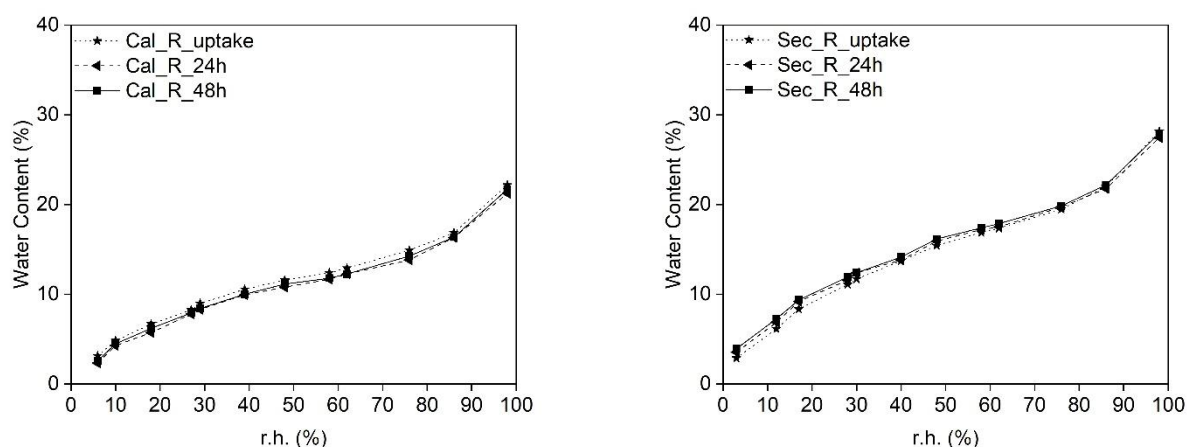


Figure 6.3: Water content as function of r.h. (%), Calcigel Raw (left) and Secursol UHP Raw (right)

Figures 6.4 present the relationship between r.h. and water content (%) for Na⁺- and K⁺-homoionic saturated montmorillonite, respectively, derived from both Caligel and Secursol UHP. Both Na⁺- and K⁺-homoionic saturated montmorillonites exhibit a progressive increase in water content with increasing relative humidity. At low r.h. (<30%), limited water adsorption occurs primarily through surface interactions with exchangeable cations and basal oxygen atoms. As relative humidity increases beyond 50%, water uptake accelerates due to multilayer adsorption and the formation of hydration shells around interlayer cations. At high relative humidity (>90%), both systems approach equilibrium, indicating near-saturation of available adsorption sites and interlayer regions.

The Na⁺-homoionic saturated montmorillonites consistently exhibit higher water contents across all r.h. levels compared to their K⁺ counterparts. This behaviour can be attributed to the greater hydration energy and smaller ionic radius of Na⁺ ions, which favour stronger electrostatic attraction with water molecules. Consequently, Na⁺ ions promote interlayer expansion and the formation of one or two hydration layers (1W-2W), resulting in stepwise swelling behaviour. In contrast, K⁺-homoionic saturated montmorillonite shows limited water adsorption and negligible swelling. The larger ionic radius and lower hydration energy of K⁺ cause it to be more tightly fixed within hexagonal cavities on the silicate surface, reducing interlayer accessibility for water molecules. This leads to the formation of a single, weakly hydrated layer and a more stable, non-expanding structure. A slight increase in water content is observed from uptake to 24 h and 48 h, particularly at intermediate humidity levels (40–80% r.h.). This indicates that water diffusion into interlayer and microporous regions occurs gradually until equilibrium is reached.

Although both Caligel and Secursol UHP samples exhibit similar adsorption trends, Secursol UHP samples consistently demonstrate higher water content at equivalent r.h. values, regardless of cation type. This difference is likely due to the higher CEC, which increase the number of active sites available for water adsorption. Na⁺-homoionic saturated montmorillonite is more reactive and exhibits stronger water-clay interactions than K⁺-homoionic saturated montmorillonite.

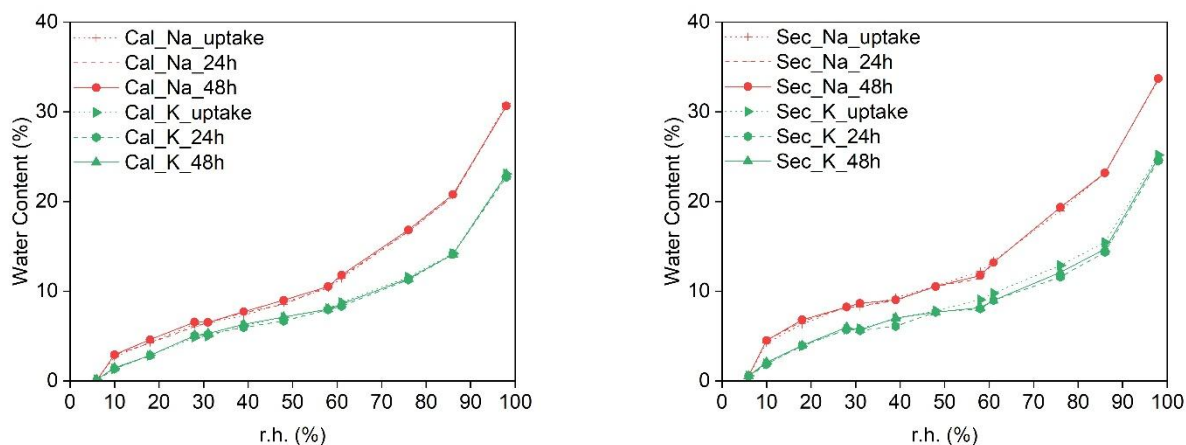


Figure 6.4: Water content as function of r.h. (%) of monovalent Caligel (left) and Secursol UHP (right)

The water sorption behaviour of Caligel and Secursol UHP exchanged with Ca²⁺ and Mg²⁺ ions were evaluated as a function of r.h. and equilibration time (Figures 6.5). In both materials, the water content increased progressively with rising relative humidity. Mg²⁺-exchanged samples consistently exhibited higher water contents than their Ca²⁺ counterparts across the entire humidity range. This behaviour can be attributed to the higher hydration energy and smaller ionic radius of Mg²⁺, which promote

stronger electrostatic interactions with water molecules and allow the formation of more stable hydration shells. Secursol UHP samples generally displayed slightly higher equilibrium water contents than Calcigel at equivalent humidity levels. Across both systems, the water content increased smoothly from approximately 5-10% at low humidity ($\leq 20\%$ r.h.) to around 30-35% at near-saturation conditions ($\approx 95\%$ r.h.). The consistent trends across both Ca^{2+} and Mg^{2+} variants confirm that water sorption is primarily governed by relative humidity.

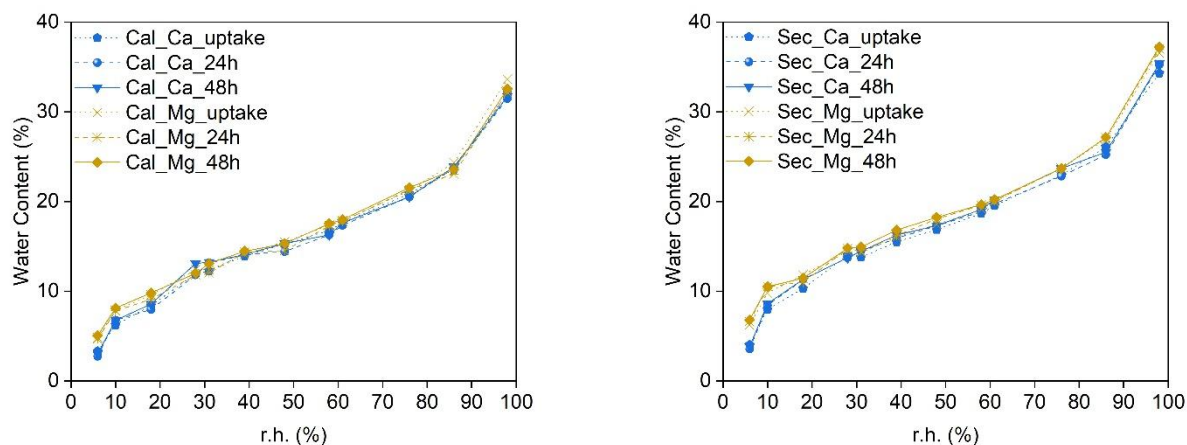


Figure 6.5: Water content as function of r.h. (%) of divalent, Calcigel (left) and Secursol UHP (right)

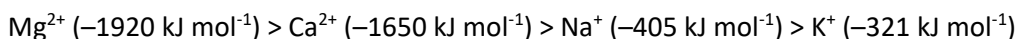
6.3.5 Number of Waters as Function of Relative Humidity

The variation of water content and amount of water molecules with relative humidity (r.h.) for Calcigel and Secursol UHP samples in 48 h and 200 °C equilibrium is presented in Figures 6.6. Both systems exhibited a gradual increase in water content with rising relative humidity. At low humidity ($<60\%$ r.h.), the increase was modest, reflecting initial monolayer adsorption of water molecules at active sites. Beyond 80% r.h., a steeper rise was observed, indicating the onset of multilayer adsorption and possible capillary condensation within interlayer and pore spaces.

At near-saturation conditions (95-100% r.h.), the total water content reached approximately 30-35%, corresponding to ~ 20 – 25 H_2O molecules per formula unit, depending on the exchanged cation. This demonstrates the strong hygroscopic nature of both clays and the crucial role of cation type in determining their hydration capacity.

The extent of water uptake varied significantly with the type of exchangeable cation. The general order of hygroscopicity was: $\text{Mg}^{2+} \approx \text{Ca}^{2+} > \text{R} > \text{Na}^+ > \text{K}^+$. The divalent cations (Mg^{2+} and Ca^{2+}) yielded the highest water uptakes across the entire humidity range. This is attributed to their strong hydration energies and high charge densities, which promote stronger electrostatic interactions with water molecules and enable the formation of multiple hydration shells within the interlayer spaces. Among the monovalent cations, the Na^+ -exchanged samples retained more water than K^+ -exchanged ones. This is consistent with the higher hydration enthalpy and smaller ionic radius of Na^+ , which allow it to form a larger and more stable hydration sphere. In contrast, K^+ , with its lower hydration energy, binds water less effectively, leading to the lowest overall sorption capacity among the cation series. The Raw samples exhibited intermediate water contents, suggesting a mixed or partially substituted interlayer composition containing both monovalent and divalent exchangeable cations.

The observed hydration trend closely follows the known ionic hydration enthalpy sequence (Atkins and Paula, 2006) at 298 K:



This correlation confirms that cations with higher hydration energies promote stronger water retention due to their greater affinity for polar water molecules.

Although both materials displayed similar trends, Secursol UHP consistently exhibited slightly higher water contents than Calcigel at equivalent r.h. levels. Secursol UHP samples smoother increase in water content and higher overall uptake suggest that it possesses a more open or porous microstructure, allowing easier access of water to interlayer and external adsorption sites. In contrast, Calcigel samples showed slightly lower total water contents and more distinct separation between the individual cation curves.

The right-hand axis in both figures shows the corresponding number of water molecules per formula unit ($n\text{H}_2\text{O}$). A nearly linear relationship was observed between water content and hydration number across the entire humidity range, with $n\text{H}_2\text{O}$ values reaching up to ~ 25 for the most hydrated samples (Mg^{2+} and Ca^{2+}) at high humidity. This trend reflects the progressive hydration of interlayer cations, which can be divided into three regimes: Low r.h. ($\leq 30\%$) - Formation of the primary hydration shell around interlayer cations. Intermediate r.h. (30-70%) - Expansion of secondary hydration shells and gradual swelling of interlayer spaces. High r.h. ($\geq 80\%$) - Multilayer adsorption and condensation of water within pores and interlayer. The close overlap of the Mg^{2+} and Ca^{2+} curves confirm similar hydration behaviours for these divalent cations, though Mg^{2+} tends to attract slightly more water due to its smaller ionic radius and higher hydration energy.

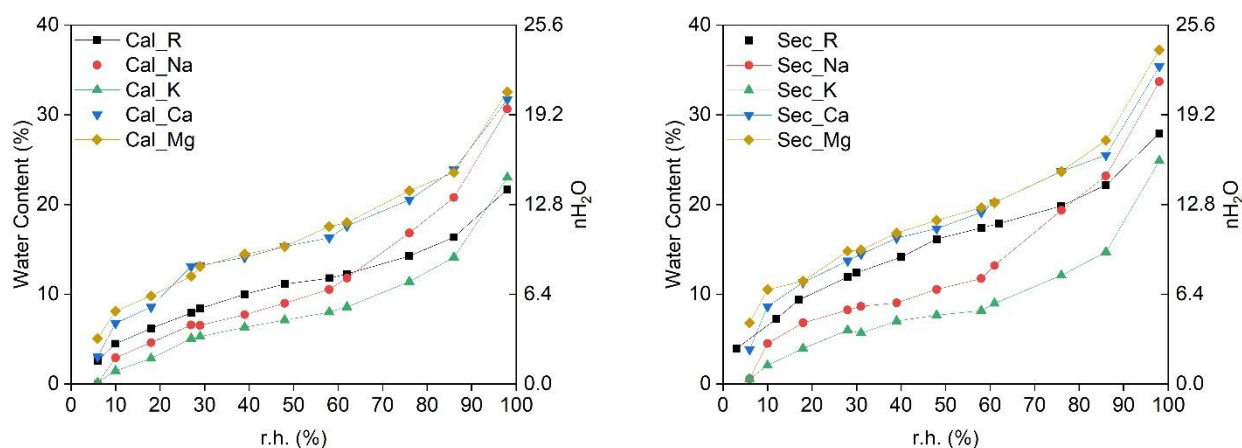


Figure 6.6: Water content and number of water molecules as function of r.h. (%) with temperature 200 °C, Calcigel (left) and Secursol UHP (right)

Water adsorption in saturated montmorillonite increases with rising r.h., leading to significant swelling due to the layered structure and interlayer water uptake. The adsorption process involves physical phenomena, like multimolecular adsorption, and is influenced by the type of exchangeable cation within the clay layers, which affects the interaction strength and the stepwise nature of swelling at different r.h. levels. Cations with higher hydration energy, such as Mg^{2+} , exhibit continuous swelling, whereas cations like Na^{+} and K^{+} show stepwise changes in basal spacing as water layers accumulate.

Na⁺-homoionic saturated montmorillonite absorbs a lot of water at high r.h. because its 2:1 layered structure and weakly bound, mobile Na⁺ interlayer cations allow for the insertion of multiple layers of water molecules into the interlayer space. At higher r.h., more water molecules are available to hydrate the Na⁺ cations, leading to the continuous expansion of the basal spacing as water molecules form hydration layers. K⁺-homoionic saturated montmorillonite has a lower water content than Na⁺-homoionic saturated montmorillonite at high r.h. because the larger potassium (K⁺) ions inhibit swelling, leading to a more restricted water uptake and lower hydration of the interlayer space. Na⁺-homoionic saturated montmorillonite, with its smaller, more strongly hydrating sodium (Na⁺) ions, can accommodate more water molecules within its interlayer spaces at higher humidity.

In low r.h., K⁺-homoionic saturated montmorillonite has the lowest water content, followed by Na⁺, Ca²⁺, and Mg²⁺-homoionic saturated montmorillonite. This is because K⁺ ions have low hydration energy, reducing the amount of interlayer water held in sample, while Mg²⁺ and Ca²⁺ ions, with higher hydration energies, can strongly attract and retain water molecules. Na⁺ and K⁺-homoionic saturated montmorillonite differ in their hydration behaviour, which Na⁺-homoionic saturated montmorillonite continues to absorb interlayer water and expand, while K⁺-homoionic saturated montmorillonite absorbs minimal water into its interlayers and remains largely non-expandable. This is because K⁺ ions, being larger and weakly hydrated, prevent water molecules from easily entering the interlayer space, unlike the more readily hydrated Na⁺ ions.

6.3.6 Water-Vapour Sorption Isotherms and Hysteresis

Water-vapour sorption isotherms were used to characterise and compare the hydration behaviour of raw and Na⁺-, K⁺-, Ca²⁺-, and Mg²⁺-homoionic saturated montmorillonite samples obtained from Calcigel and Secursol UHP bentonites. The variation in water content with relative humidity (r.h.) was examined to assess water uptake, adsorption–desorption hysteresis, and differences in overall sorption patterns. Particular emphasis was placed on evaluating the respective contributions of exchangeable cations and parent-material characteristics to water retention under varying humidity conditions. While the isotherms reveal differences in macroscopic water-sorption behaviour, the identification of specific interlayer hydration states requires further structural investigation using X-ray diffraction (XRD) under controlled relative-humidity conditions. Accordingly, combining gravimetric sorption analysis with structural characterisation provides a more comprehensive understanding of how exchangeable cations and intrinsic material properties influence the hydration behaviour of montmorillonite.

The water-vapour sorption isotherm of Cal_R exhibits a gradual but nonlinear increase in water content, from approximately 4–5% at low relative humidity (r.h.) to 21.2% at 97% r.h. (Figure 6.7, left). Unlike Sec_R, Cal_R does not exhibit a pronounced increase in water uptake around 26–30% r.h. Instead, its water content increases progressively across most of the investigated humidity range. Nevertheless, a gradual increase in gravimetric water content does not necessarily indicate continuous interlayer expansion, as montmorillonite may undergo discrete transitions between hydration states that require structural characterisation for identification (Dios Cancela et al., 1997).

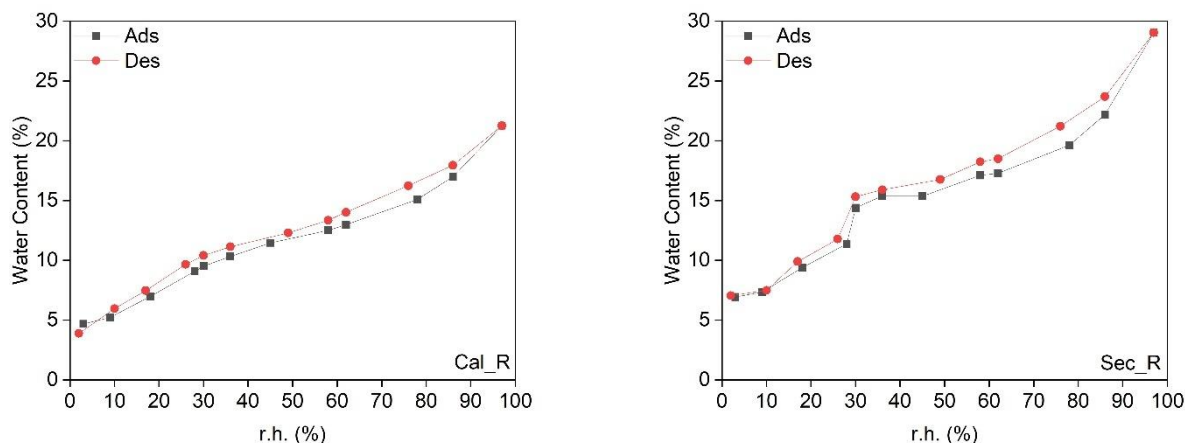


Figure 6.7: Water-Vapour Sorption Isotherms of Calcigel Raw (left) and Secursol UHP Raw (right)

The adsorption and desorption branches of Cal_R also exhibit hysteresis. At the lowest measured humidity levels, the desorption branch initially lies below the adsorption branch, with the curves appearing to intersect at approximately 5–7% r.h. Beyond this region, desorption generally yields higher water contents than adsorption, and both branches converge at approximately 21.2% water content at 97% r.h. This behaviour suggests that water retention depends on the hydration pathway and may involve interlayer reorganisation, interactions between water molecules and mineral surfaces, and water retention within the pore network.

In comparison, the water-vapour sorption isotherm of Sec_R exhibits a greater overall increase in water content, rising from approximately 7% at low r.h. to 29% at 97% r.h. (Figure 6.7, right). Its sorption profile is distinctly nonlinear, with a pronounced increase around 26–30% r.h., followed by a more gradual rise at intermediate humidity levels and a further marked increase above approximately 86% r.h. These changes indicate that water uptake responds differently across the humidity range and may reflect variations in the relative contributions of different sorption processes. In montmorillonite, gravimetric water uptake can increase progressively even when changes in basal spacing occur discretely as interlayer hydration states evolve (Dios Cancela et al., 1997).

The adsorption and desorption branches of Sec_R exhibit pronounced hysteresis, with the desorption branch generally lying above the adsorption branch throughout much of the intermediate-to-high humidity range. Both branches converge at approximately 29% water content at 97% r.h. This pattern indicates path-dependent water retention during hydration and dehydration. Potential contributing mechanisms include interlayer cation hydration, rearrangement of interlayer water molecules, hydrogen-bond formation, and water retention within pores. At high humidity, multilayer adsorption on external surfaces and potentially capillary condensation may also contribute. Nevertheless, the relative importance of these processes cannot be determined from the gravimetric isotherm alone (Cases et al., 1997; Wang et al., 2025).

A comparison of the two samples reveals distinct water-vapour sorption behaviours. Sec_R generally exhibits greater water uptake than Cal_R across much of the investigated humidity range, reaching approximately 29% water content at 97% r.h., compared with 21.2% for Cal_R. This difference of 7.8 percentage points indicates a higher overall water content in Sec_R under the final measured condition. The two samples also differ in their sorption profiles: Sec_R exhibits a marked increase around 26–30% r.h. and another pronounced rise above approximately 86% r.h., whereas Cal_R

displays a comparatively gradual response. These differences may be associated with variations in mineralogical composition, layer-charge distribution, particle aggregation, and pore structure; however, the isotherms alone do not establish differences in specific surface area, cation-exchange capacity, or interlayer swelling capacity.

Both samples exhibit adsorption–desorption hysteresis, demonstrating that water retention depends on hydration history. Previous studies have established the influence of exchangeable cations on montmorillonite hydration and interlayer expansion, while molecular simulations have linked hysteresis in Ca-montmorillonite to cation hydration and hydrogen-bond formation (Cases et al., 1997; Wang et al., 2025). These findings provide a plausible framework for interpreting the observed behaviour but do not identify the dominant mechanisms in either untreated bentonite. The convergence of the adsorption and desorption branches at 97% r.h. indicates similar total water contents at the final measured condition for each sample, but it does not demonstrate identical water distributions or interlayer structures. Sec_R exhibits greater water uptake and more pronounced variations in its sorption profile, whereas Cal_R shows a more gradual response.

The water-vapour sorption isotherm of Cal_Na exhibits a progressive but nonlinear increase in water content, from approximately 1.8% at 3% relative humidity (r.h.) during adsorption to 22.8% at 97% r.h. (Figure 6.8, left). The desorption branch increases from approximately 2.4% at 2% r.h. to the same final water content. Changes in slope are apparent around 26–36%, 58–62%, and 78–86% r.h., indicating variations in the overall sorption response across the investigated humidity range. However, these features cannot independently establish transitions between specific interlayer hydration states, as gravimetric water uptake may reflect contributions from interlayer hydration, external-surface adsorption, and water retention within interparticle and interaggregate pores.

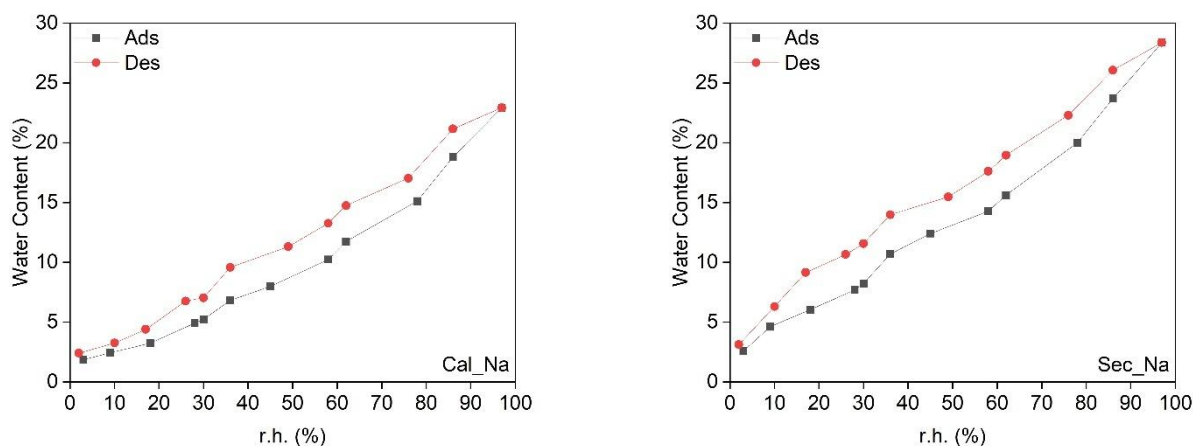


Figure 6.8: Water-Vapour Sorption Isotherms of Cal_Na (left) and Sec_Na (right)

The adsorption and desorption branches of Cal_Na exhibit hysteresis, with the desorption branch generally lying above the adsorption branch across several humidity intervals. The separation between the branches reaches approximately 2–3 percentage points in some regions, before they converge at 97% r.h. This behaviour indicates that water retention depends on the hydration pathway and may involve changes in interlayer hydration, interactions between water molecules and mineral surfaces, and pore-water retention. Nevertheless, the relative contributions of these mechanisms cannot be distinguished from the gravimetric isotherm alone (Bérend et al., 1995). Identifying specific hydration states, such as 0W, 1W, and 2W, requires complementary structural characterisation using X-ray

diffraction (XRD) under controlled relative-humidity conditions. In particular, analysis of the basal spacing, together with modelling of the 001 reflection profiles, would provide a stronger basis for identifying coexisting hydration states (Ferrage et al., 2005).

In comparison, the water-vapour sorption isotherm of Sec_Na exhibits a more pronounced nonlinear increase in water content, rising from approximately 2.5% at 3% r.h. to 28.3% at 97% r.h. during adsorption (Figure 6.8, right). The desorption branch increases from approximately 3.1% at 2% r.h. to the same final water content. Pronounced changes in slope occur across several humidity intervals, particularly at 10–36% and 76–86% r.h., indicating a more variable overall sorption response than that observed for Cal_Na. These variations may reflect changing contributions from Na⁺ hydration within the interlayers, external-surface adsorption, and water retention in interparticle and interaggregate pores (Cases et al., 1992; Bérend et al., 1995).

The adsorption and desorption branches of Sec_Na also display hysteresis, with the desorption branch generally lying above the adsorption branch. The separation reaches approximately 3–3.5 percentage points in some intermediate-humidity regions before both branches converge at 97% r.h. This behaviour indicates path-dependent water retention during hydration and dehydration. Although interlayer cation hydration, the rearrangement of interlayer water molecules and pore-water retention may contribute to the observed hysteresis.

A comparison of the two samples reveals differences in both water uptake and sorption behaviour despite their common exchangeable cation. At 97% r.h., Sec_Na reaches approximately 28.3% water content, compared with 22.8% for Cal_Na, representing a difference of 5.5 percentage points. Sec_Na also exhibits more pronounced changes in slope and greater hysteresis in some humidity intervals. These observations indicate that the two bentonites respond differently to changes in relative humidity. The higher water content of Sec_Na may be associated with differences in mineralogical composition, layer-charge distribution, particle aggregation, or pore structure. Although Na⁺ influences interlayer hydration and crystalline swelling, the isotherms alone cannot determine the relative contributions of these factors or establish differences in specific surface area, cation-exchange capacity, or interlayer swelling capacity.

Both samples show adsorption–desorption hysteresis, confirming that their water-retention behaviour depends on hydration history. The convergence of the adsorption and desorption branches at 97% r.h. indicates comparable total water contents at the final measured condition for each sample, but does not demonstrate identical water distributions or interlayer configurations. Sec_Na exhibits greater water uptake and more pronounced variations in its sorption profile than Cal_Na.

The water-vapour sorption isotherm of Cal_K exhibits a progressive but nonlinear increase in water content, from approximately 1.8% at 3% relative humidity (r.h.) during adsorption to 17.2% at 97% r.h. (Figure 6.9, left). The desorption branch rises from approximately 2.3% at 2% r.h. to the same final water content. Variations in the isotherm slope occur around 26–36%, 45–62%, and 76–86% r.h., indicating a non-uniform sorption response across the investigated humidity range. Water uptake may involve interlayer hydration, adsorption on external mineral surfaces, and water retention within interparticle and interaggregate pores.

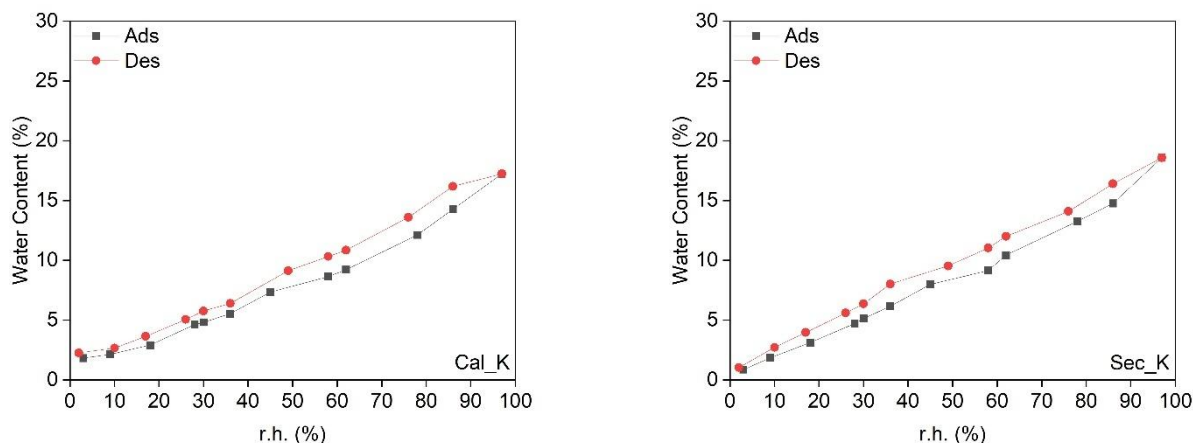


Figure 6.9: Water-Vapour Sorption Isotherms of Cal_K (left) and Sec_K (right)

The adsorption and desorption branches of Cal_K exhibit hysteresis, with the desorption branch generally lying above the adsorption branch across several intermediate-to-high relative humidity intervals. The separation reaches approximately 1.5–2 percentage points in some regions before both branches converge at 97% r.h. This behaviour indicates that water retention depends on the hydration pathway and may reflect differences in interlayer hydration, interactions between water molecules and mineral surfaces, and pore-water retention. Hysteresis is particularly apparent around 76–86% r.h. Nevertheless, its magnitude should be quantified by comparing water-content values at matched humidity levels, rather than relying solely on visual estimates. Furthermore, gravimetric measurements alone cannot identify the molecular mechanisms responsible for the observed hysteresis. Quantitative modelling of the 001 XRD reflection profiles would help determine the relative proportions of coexisting interlayer hydration states (Bérend et al., 1995; Ferrage et al., 2005).

In comparison, the water-vapour sorption isotherm of Sec_K displays a nonlinear increase in water content, from approximately 0.8% at 3% r.h. during adsorption to 18.6% at 97% r.h. (Figure 6.9, right). The desorption branch increases from approximately 1.0% at 2% r.h. to the same final water content. Changes in slope are apparent around 26–36%, 45–62%, and 76–86% r.h., indicating variations in the overall sorption response. As in Cal_K, these features may reflect the combined contributions of interlayer hydration, external-surface adsorption, and water retention within interparticle and interaggregate pores. The exchangeable K⁺ ions tend to associate closely with siloxane surfaces, potentially restricting interlayer expansion relative to Na⁺-saturated montmorillonite (de Pablo, 2004; Endo & Sato, 2024).

The adsorption and desorption branches of Sec_K also exhibit hysteresis, with the desorption branch generally lying above the adsorption branch. Differences of approximately 1–2 percentage points occur across several humidity intervals before both branches converge at 97% r.h. This pattern indicates path-dependent water retention, potentially associated with interlayer reorganisation, water–surface interactions, and pore-water retention. Although the overall hysteretic behaviour resembles that of Cal_K, the magnitude of the separation between the branches differs across the humidity range, suggesting differences in their macroscopic water-retention responses.

A comparison of the two samples reveals broadly similar isotherm shapes but differences in water uptake and hysteresis. At 97% r.h., Sec_K reaches approximately 18.6% water content, compared with 17.2% for Cal_K, representing a difference of 1.4 percentage points. Although Cal_K exhibits slightly

higher initial adsorption values, Sec_K generally retains more water across much of the intermediate-to-high humidity range. These differences may reflect variations in mineralogical composition, layer-charge distribution, particle aggregation, and pore structure, rather than the exchangeable cation alone. Cal_K also exhibits more pronounced hysteresis in selected high-humidity intervals, particularly around 76–86% r.h. These observations indicate that the two materials differ in their macroscopic sorption behaviour despite sharing the same dominant exchangeable cation.

Compared with their corresponding Na⁺-saturated counterparts, both K⁺-saturated samples exhibit lower final water contents. For Secursol UHP, the water content decreases from 28.3% for Sec_Na to 18.6% for Sec_K, whereas for Calcigel, it decreases from 22.8% for Cal_Na to 17.2% for Cal_K. These differences are consistent with the generally more restricted interlayer swelling of K⁺-saturated montmorillonite compared with its Na⁺-saturated counterpart, although gravimetric water content alone does not quantify crystalline expansion (de Pablo, 2004; Endo & Sato, 2024). Sec_K exhibits slightly greater water uptake at high relative humidity, whereas Cal_K displays more pronounced hysteresis in selected humidity intervals.

The water-vapour sorption isotherm of Cal_Ca exhibits a progressive but nonlinear increase in water content, from approximately 6.0% at low relative humidity (r.h.) to 26.1% at 97% r.h. (Figure 6.10, left). Variations in the slope are apparent around 18–36% and 62–86% r.h., indicating a non-uniform sorption response across the investigated humidity range. However, these changes do not independently establish transitions between specific interlayer hydration states. Water uptake may involve interlayer Ca²⁺ hydration, adsorption on external mineral surfaces, and water retention within interparticle and interaggregate pores. Although Ca²⁺ hydration can influence interlayer swelling, gravimetric measurements alone cannot quantify the individual contributions of these processes (Dios Cancela et al., 1997; Wang et al., 2025).

The adsorption and desorption branches of Cal_Ca exhibit hysteresis, with the desorption branch generally lying above the adsorption branch across several humidity intervals. The apparent separation between the branches is approximately 1–2 percentage points in some regions, particularly around 76–86% r.h., before both branches converge at 97% r.h. This behaviour indicates that water retention depends on the hydration pathway and may reflect differences in interlayer hydration, water–surface interactions, and pore-water retention. Nevertheless, the magnitude of hysteresis should be quantified using water-content values at matched relative humidity levels rather than visual estimates alone. Molecular modelling has shown that interlayer Ca²⁺ hydration and hydrogen-bond formation can contribute to hysteresis in Ca-montmorillonite, although the dominant mechanisms in Cal_Ca remain unconfirmed (Wang et al., 2025).

In comparison, the water-vapour sorption isotherm of Sec_Ca displays a nonlinear increase in water content from approximately 5.7% at low r.h. to 29.0% at 97% r.h. (Figure 6.10, right). A pronounced change in slope occurs between approximately 10% and 36% r.h., followed by a more gradual increase in water uptake at higher humidity levels. This profile differs from the comparatively gradual response of Cal_Ca and suggests a distinct macroscopic sorption behaviour. Nevertheless, changes in the isotherm slope cannot be assigned directly to transitions between the 0W, 1W, and 2W interlayer hydration states. Controlled-r.h. X-ray diffraction (XRD), particularly analysis of the basal spacing, d_{001} , and modelling of the 001 reflection profiles, is required to identify coexisting hydration states (Cases et al., 1997; Ferrage et al., 2005).

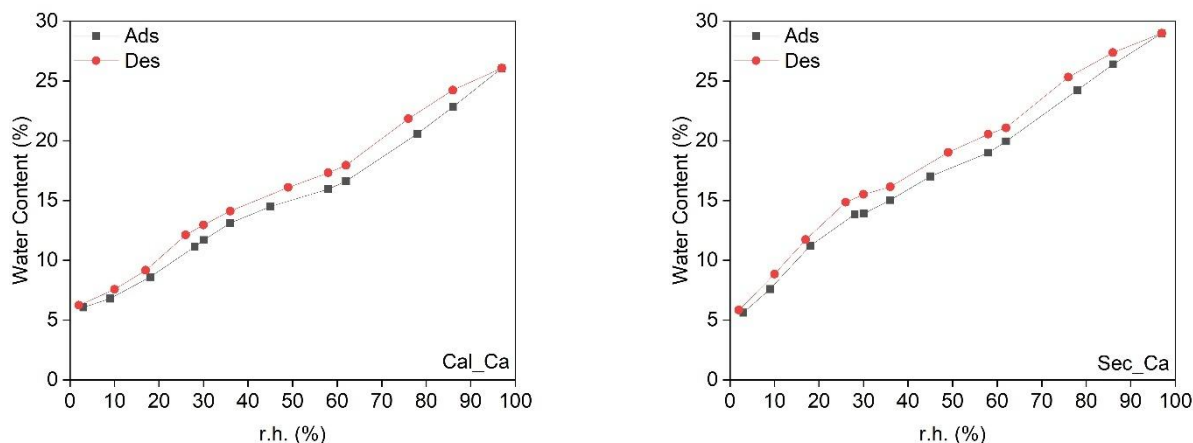


Figure 6.10: Water-Vapour Sorption Isotherms of Cal_Ca (left) and Sec_Ca (right)

The adsorption and desorption branches of Sec_Ca also exhibit hysteresis, with desorption generally yielding higher water contents than adsorption before both branches converge at 97% r.h. This behaviour suggests path-dependent water retention, potentially involving interlayer Ca^{2+} hydration, surface adsorption, and water retention within the pore network. However, the relative contributions of these processes cannot be distinguished from the gravimetric isotherm alone. Complementary structural analysis is therefore necessary to establish whether the observed sorption behaviour is associated with changes in interlayer hydration, external-surface adsorption, or pore-water retention.

A comparison of the two samples reveals differences in water uptake and the shape of their sorption profiles despite their common exchangeable cation. At 97% r.h., Sec_Ca reaches approximately 29.0% water content, compared with 26.1% for Cal_Ca, representing a difference of 2.9 percentage points. Although Cal_Ca exhibits slightly higher water content at low relative humidity, Sec_Ca generally retains more water across much of the subsequent humidity range. Sec_Ca also displays a pronounced change in slope around 10–36% r.h., whereas Cal_Ca exhibits a more gradual response, with slope variations around 18–36% and 62–86% r.h. These differences may reflect variations in mineralogical composition, layer-charge distribution, particle aggregation, and pore structure. However, the isotherms alone cannot establish differences in crystalline swelling capacity, specific surface area, or cation-exchange capacity.

Both samples exhibit adsorption–desorption hysteresis, confirming that water retention depends on hydration history. The separation between the branches is particularly apparent for Cal_Ca around 76–86% r.h.; however, quantitative comparisons require matched-humidity measurements. Although previous molecular modelling supports the potential contribution of interlayer Ca^{2+} hydration and hydrogen-bond formation to hysteresis, the mechanisms governing the behaviour of these two bentonites remain uncertain (Wang et al., 2025). The convergence of the adsorption and desorption branches at 97% r.h. indicates similar total water contents at the final measured condition for each sample, but does not establish identical water distributions or interlayer structures. Sec_Ca exhibits greater water uptake at high relative humidity, whereas Cal_Ca shows a comparatively gradual sorption response and more visibly pronounced hysteresis in selected humidity intervals.

The water-vapour sorption isotherm of Cal_Mg exhibits a nonlinear increase in water content, from approximately 7.7% at low relative humidity (r.h.) to 26.7% at 97% r.h. (Figure 6.11, left). Variations in the isotherm slope occur around 17–36%, 45–62%, and 76–86% r.h., indicating a non-uniform sorption

response across the investigated humidity range. Water uptake may involve interlayer Mg^{2+} hydration, adsorption on external mineral surfaces, and water retention within interparticle and interaggregate pores. Although Mg^{2+} has a strong affinity for water, the total gravimetric water content does not directly quantify the amount of water coordinated to the cation or the extent of crystalline swelling (Dios Cancela et al., 1997).

The adsorption and desorption branches of Cal_Mg exhibit hysteresis, with the desorption branch generally lying above the adsorption branch, particularly at intermediate-to-high relative humidity. Both branches converge at the final measured condition of 97% r.h. This behaviour indicates that water retention depends on the hydration pathway and may reflect differences in interlayer hydration, water–surface interactions, and pore-water retention. Structural characterisation is therefore necessary to distinguish changes in interlayer hydration from other sources of water uptake.

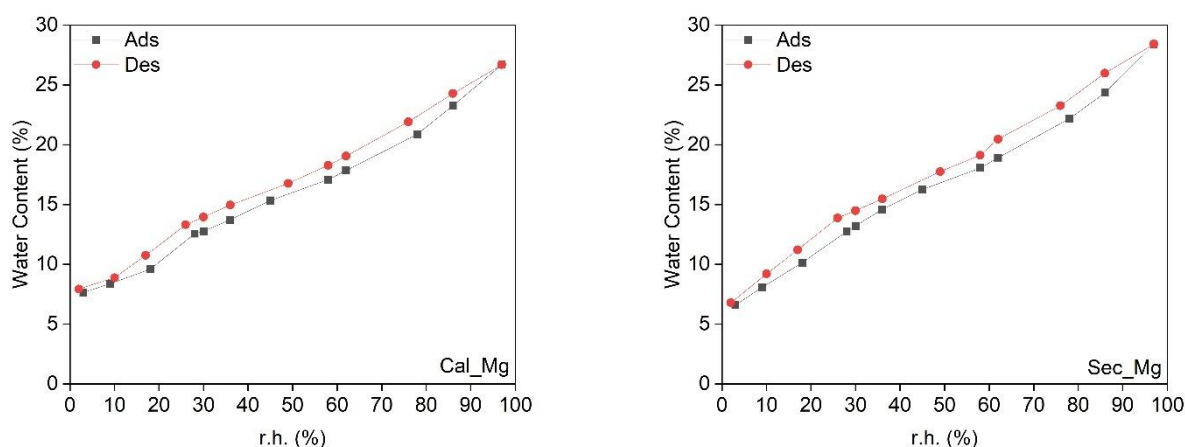


Figure 6.11: Water-Vapour Sorption Isotherms of Cal_Mg (left) and Sec_Mg (right)

In comparison, the water-vapour sorption isotherm of Sec_Mg exhibits a nonlinear increase in water content from approximately 6.5% at low r.h. to 28.4% at 97% r.h. (Figure 6.11, right). A pronounced change in slope occurs around 17–30% r.h., followed by continued water uptake at higher humidity. The relatively high initial water content may reflect contributions from interlayer Mg^{2+} hydration, external-surface adsorption, and water retention within the pore network. However, changes in the isotherm slope do not independently establish transitions between the 0W, 1W, and 2W interlayer hydration states. Identifying coexisting hydration states requires complementary structural analysis using X-ray diffraction (XRD) under controlled relative-humidity conditions, particularly through analysis of the basal spacing, d_{001} , and modelling of the 001 reflection profiles (Cases et al., 1997; Ferrage et al., 2005).

The adsorption and desorption branches of Sec_Mg also exhibit hysteresis, with desorption generally producing higher water contents than adsorption before both branches converge at 97% r.h. This pattern indicates path-dependent water retention during hydration and dehydration. Potential contributing mechanisms include changes in interlayer hydration, rearrangement of interlayer water molecules, hydrogen-bond formation, and water retention within pores.

A comparison of the two samples reveals differences in water uptake across the relative-humidity range despite their common exchangeable cation. At low r.h., Cal_Mg exhibits a higher water content than Sec_Mg, with initial values of approximately 7.7–8.0% and 6.5–6.8%, respectively. However,

Sec_Mg generally retains more water across much of the intermediate-to-high humidity range. At 97% r.h., Sec_Mg reaches approximately 28.4% water content, compared with 26.7% for Cal_Mg, representing a difference of 1.7 percentage points. Their distinct isotherm profiles may reflect differences in mineralogical composition, layer-charge distribution, particle aggregation, and pore structure rather than the exchangeable cation alone.

Both samples exhibit adsorption–desorption hysteresis, with the desorption branch generally lying above the adsorption branch before convergence at 97% r.h. The separation is particularly evident at high humidity, although its magnitude should be quantified using water-content values measured at matched r.h. values rather than visual estimates alone. Previous studies of homoionic montmorillonites have demonstrated the influence of exchangeable cations on water adsorption, interlayer hydration, and structural changes (Cases et al., 1997; Dios Cancela et al., 1997). These findings provide a scientific basis for interpreting the observed behaviour, but the specific mechanisms operating in Cal_Mg and Sec_Mg remain to be confirmed. Cal_Mg retains more water at low humidity, whereas Sec_Mg exhibits greater water uptake at high humidity. These differences highlight the role of parent-material characteristics in determining sorption behaviour, even when both materials are saturated with Mg^{2+} .

More broadly, the water-vapour sorption isotherms of the ten samples demonstrate that water uptake depends on the exchangeable cation, relative humidity, and characteristics of the parent material. At 97% r.h., Secursol UHP generally exhibits higher water contents than the corresponding Calcigel samples. Among the homoionic forms, K^+ -homoionic saturated montmorillonite exhibits the lowest final water content in both materials, whereas the Na^+ -, Ca^{2+} -, and Mg^{2+} -homoionic saturated montmorillonite forms show greater water uptake, although their relative rankings vary between the two bentonites. The adsorption–desorption hysteresis observed across the samples further demonstrates that water retention depends on hydration history. Variations in isotherm slopes indicate differences in the macroscopic sorption response across the humidity range; however, these features alone cannot establish specific interlayer hydration transitions.

Overall, the results highlight the combined influence of exchangeable cations and parent-material characteristics on water-vapour sorption. Integrating gravimetric sorption measurements with mineralogical and chemical characterisation, pore analysis, and XRD under controlled relative-humidity conditions would provide a stronger basis for distinguishing interlayer hydration from external-surface adsorption and pore-water retention. In particular, tracking d_{001} and modelling the 001 reflection profiles would help clarify the structural origins of the differences in water-vapour sorption between the two samples (Ferrage et al., 2005; Morodome & Kawamura, 2009).

6.3.7 XRD Analysis and Hysteresis

This section presents the XRD analysis of Calcigel Raw (Cal_R) under varying r.h. conditions to evaluate the structural response of montmorillonite during hydration and dehydration. This examined to reveal changes in d_{001} , hydration state transitions, and the reversibility of the swelling-contraction process. Figure 6.12 shows the XRD patterns of montmorillonite samples recorded at various r.h. of Calcigel Raw (Cal_R) sample during adsorption and desorption cycles. The evolution of the basal reflection (001) provides direct evidence of changes in d_{001} associated with the hydration and dehydration of the clay structure.

At low relative humidity (3–10% r.h.), the main (001) reflection appears at higher 2θ values (~ 8 – 9°), corresponding to a basal spacing of approximately 10–12 Å. This spacing represents a nearly

dehydrated or one-water-layer (1W) hydration state. The sharpness of the peak indicates a relatively well-ordered interlayer structure with limited water content. As humidity increases from 20% to 75% r.h., the (001) peak gradually shifts to lower 2θ values ($6-7^\circ$), reflecting an increase in basal spacing to around 13-15 Å. This expansion corresponds to the intercalation of additional water molecules between the silicate layers, leading to mixed hydration states (1W-2W). The broadening of the reflection peak within this range suggests partial interstratification between layers containing different numbers of water molecules. At high humidity (85-95% r.h.), the basal spacing further increases to approximately 15-16 Å, indicating the formation of a two-water-layer (2W) structure. This represents the maximum hydration state typically achievable under ambient conditions for montmorillonite. The progressive shift toward lower diffraction angles during adsorption confirms that water molecules enter the interlayer space in a stepwise manner, hydrating the exchangeable cations and expanding the lattice.

During desorption (as relative humidity decreases), the basal reflection shifts back toward higher 2θ values, signifying a contraction of the interlayer space as water is released. However, the desorption path does not exactly coincide with the adsorption path, producing a hysteresis loop. The basal spacing during desorption remains slightly larger than that of adsorption at equivalent humidity levels, indicating incomplete removal of interlayer water. This hysteresis arises from the strong binding of water molecules to interlayer cations and the formation of stable hydration shells that resist dehydration. The observed changes in d_{001} spacing confirm the presence of stepwise hydration states corresponding to discrete interlayer configurations. The swelling and contraction processes are governed primarily by the hydration energy and valence of the exchangeable cations within the interlayer.

The return of the (001) reflection to its original position at low humidity after the desorption cycle demonstrates the structural reversibility of the montmorillonite. No evidence of permanent layer collapse or delamination is observed, indicating that the hydration–dehydration cycles occur without significant alteration of the crystal framework. This reversible but hysteretic behaviour reflects the dynamic balance between cation hydration forces, van der Waals attractions between layers, and the thermodynamics of water adsorption and release. The retention of interlayer water at low humidity suggests that a fraction of water molecules remain strongly bound, likely through direct cation coordination.

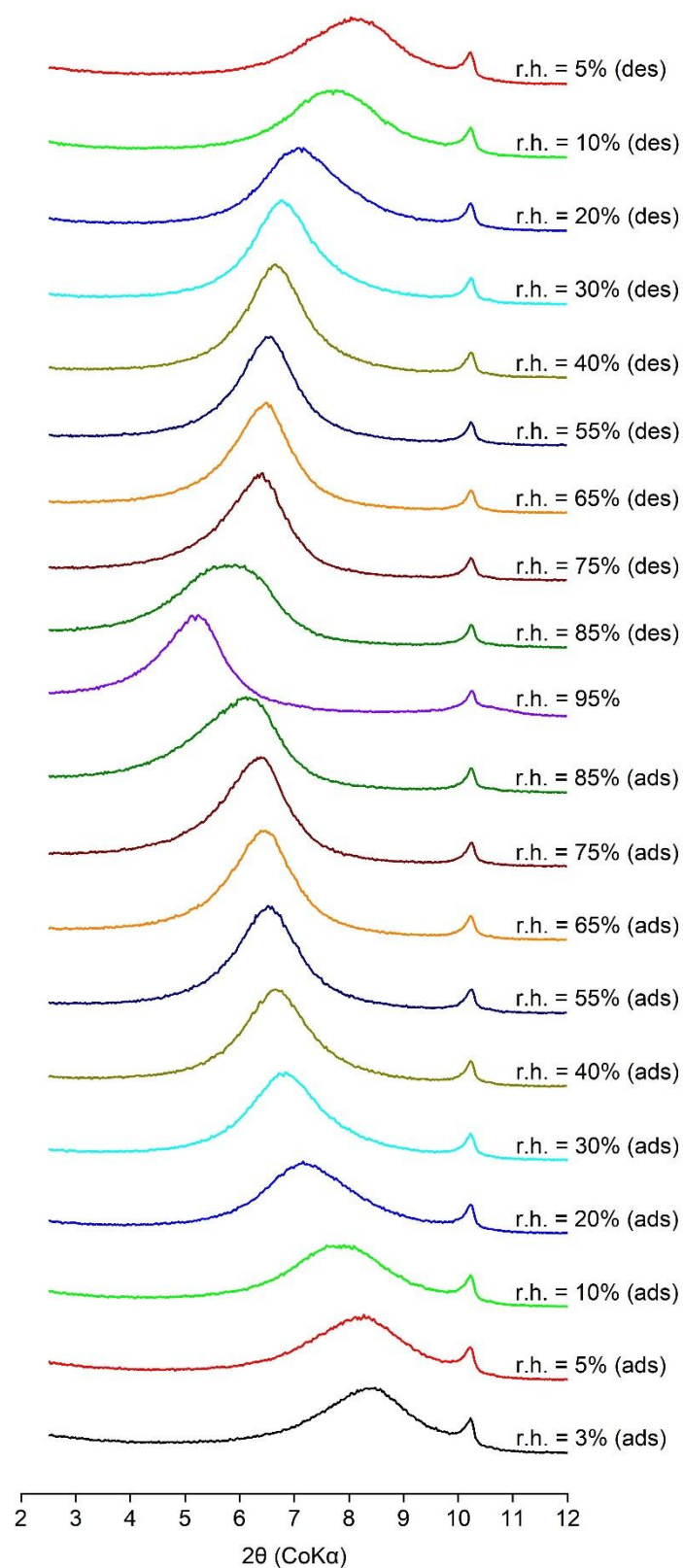


Figure 6.12: XRD isotherm of Calcigel Raw (Cal_R)

Figure 6.13 shows the relationship between d_{001} (Å) and r.h. (%) for a Cal_R during adsorption (ads) and desorption (des) cycles. The plot illustrates how the interlayer distance of the clay changes as water is absorbed and released from the structure, a direct reflection of its hydration and dehydration behaviour. As relative humidity increases, d_{001} expands from approximately 12 Å to 20 Å, corresponding to the transition from dehydrated to fully hydrated interlayer states. The expansion occurs gradually and is largely reversible, with minor hysteresis observed during desorption, indicating delayed water release and partial structural retention of hydration layers. The approximate of quantitative d_{001} assignments per hydration step are: 0W - nearly dry/dehydrated (11.8-12.2 Å, 0-5% r.h.) is minimal interlayer water which basal spacing dominated by structural hydroxyls and counterion coordination; 1W - monohydrate (12.8-14.0 Å, $\approx$ 5-30% r.h.) is a single water layer hydration layer around interlayer cations, begins as water first adsorbs and hydrates cations; 2W - bihydrate (14.8-15.6 Å, $\approx$ 30-80% r.h.) is fully developed first hydration shell(s) and formation of an ordered two-water-layer; and >2W - multilayer (18.5-20.5 Å, $\geq$ 85% r.h.) is additional water layers/partial solvation leading to large basal expansion; may include interstratified or loosely bound multilayers and capillary water.

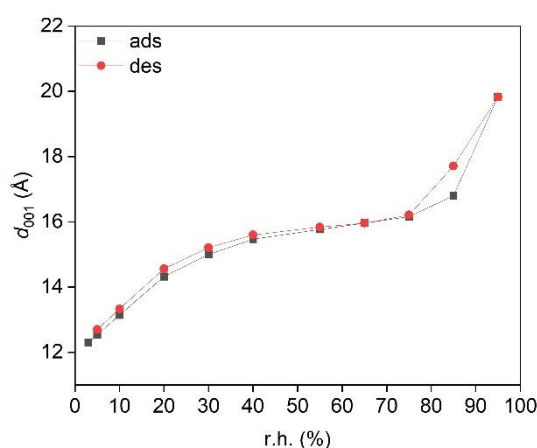


Figure 6.13: d_{001} Calcigel Raw (Cal_R) as function of r.h.

Figures 6.12 and 6.13 demonstrate that Cal_R exhibits reversible but hysteretic swelling behaviour governed by ambient humidity. The structural expansion arises from water adsorption into the interlayer galleries, where the number of water layers depends on the surrounding moisture content. The partial irreversibility upon drying implies that a fraction of interlayer water remains strongly bound to exchangeable cations or surface sites. These results confirm the characteristic humidity-dependent swelling and stepwise hydration mechanism of montmorillonite. The observed hysteresis between adsorption and desorption can also be correlated with the presence of mesoporosity in montmorillonite. At low humidity, water uptake occurs mainly within the interlayer region, producing discrete stepwise expansions in the basal spacing. As humidity increases, water also condenses within interparticle mesopores and external surfaces. These mesoporous domains retain water more strongly during drying due to capillary effects and hindered diffusion, contributing to the delayed contraction of the interlayer spacing during desorption. Consequently, the combined effects of interlayer hydration and mesopore water adsorption account for the partially reversible swelling behaviour observed in Cal_R sample.

The mineralogical complexity of Calcigel must also be considered. Published characterisation identifies smectite as its principal clay component, accompanied by mica/illite, quartz, and other minor mineral

phases (Asaad et al., 2025). The sharp reflection at approximately $2\theta = 10.2^\circ$, which remains relatively unchanged with r.h., corresponds to a basal spacing of approximately 10.1 Å for Co-K α radiation. This is consistent with a non-expandable 10 Å phase, such as mica or illite, rather than the humidity-dependent montmorillonite (001) reflection. However, this assignment remains tentative because a single reflection is insufficient for definitive mineral identification. Overall, the XRD data demonstrate progressive hydration of the smectitic fraction, ranging from predominantly 1W-like configurations at low r.h. through a 2W-dominated regime at intermediate r.h. to highly hydrated, 3W-like configurations at high r.h..

XRD patterns of Calcigel Na⁺-homoionic saturated montmorillonite (Cal_Na) exhibit humidity-dependent changes in the basal (001) reflection, reflecting water-induced expansion of the interlayer (Figure 6.14). During adsorption, the basal spacing d_{001} remains approximately 10.0 Å between 3% and 30% r.h., before increasing to 12.0 Å at 40% r.h., 13.8 Å at 55% r.h., 15.2–15.6 Å at 65–75% r.h., and 16.1 Å at 85% r.h.. At 95% r.h., it reaches approximately 19.3 Å. During desorption, d_{001} is approximately 10.0 Å at 5% r.h., 11.8–12.8 Å at 10–40% r.h., 14.9 Å at 55% r.h., 15.6–15.8 Å at 65–75% r.h., and 17.8 Å at 85% r.h.. Both branches converge at approximately 19.3 Å at 95% r.h. (Figure 6.15). These changes indicate progressive interlayer hydration and crystalline swelling, with the structural response depending on both r.h. and hydration history (Ferrage et al., 2005; Oueslati & Meftah, 2018).

The persistence of a d_{001} maximum near 10.0 Å during adsorption up to 30% r.h. is consistent with a predominantly dehydrated, zero-water-layer (0W) configuration. However, the broadening and low-angle asymmetry of the reflections at intermediate points within this interval suggest that hydration may be heterogeneous, even when the maximum remains near 10.0 Å. Expansion becomes more apparent at 40% r.h., where d_{001} reaches approximately 12.0 Å, consistent with a monohydrated (1W) configuration. Thus, the observed transition from 0W-like to 1W-like hydration occurs progressively rather than necessarily as an abrupt change at a single r.h. threshold. Its precise onset may depend on interlayer composition, layer charge, sample preparation, and equilibration conditions (Ferrage et al., 2005; Oueslati & Meftah, 2018).

Between 40% and 55% r.h., d_{001} increases from approximately 12.0 to 13.8 Å, indicating progressive hydration towards the 1W–2W transition region. At 65–75% r.h., the basal spacing reaches approximately 15.2–15.6 Å, consistent with a predominantly bihydrated (2W) configuration. The subsequent increase to 16.1 Å at 85% r.h. suggests further interlayer expansion but does not, by itself, establish the formation of a homogeneous 3W phase. During transitional hydration, different layer types may coexist within the crystallites, producing broadened or asymmetric reflections. Consequently, gradual changes in d_{001} may reflect variations in water distribution and interlayer thickness rather than the successive formation of complete water layers at every r.h. increment (Ferrage et al., 2005).

At 95% r.h., the basal spacing reaches approximately 19.3 Å, indicating extensive hydration consistent with a highly hydrated, trihydrated (3W-like) configuration. Although this value slightly exceeds the commonly reported 18–19 Å range for 3W smectite, it does not necessarily indicate a distinct or homogeneous hydration phase. Structural heterogeneity and mixed hydration states may contribute to the observed diffraction profile. Quantifying the proportions of 0W, 1W, 2W, and 3W layers would therefore require modelling of the complete XRD patterns rather than relying solely on the position of the maximum (001) reflection (Dazas et al., 2014; Ferrage et al., 2005).

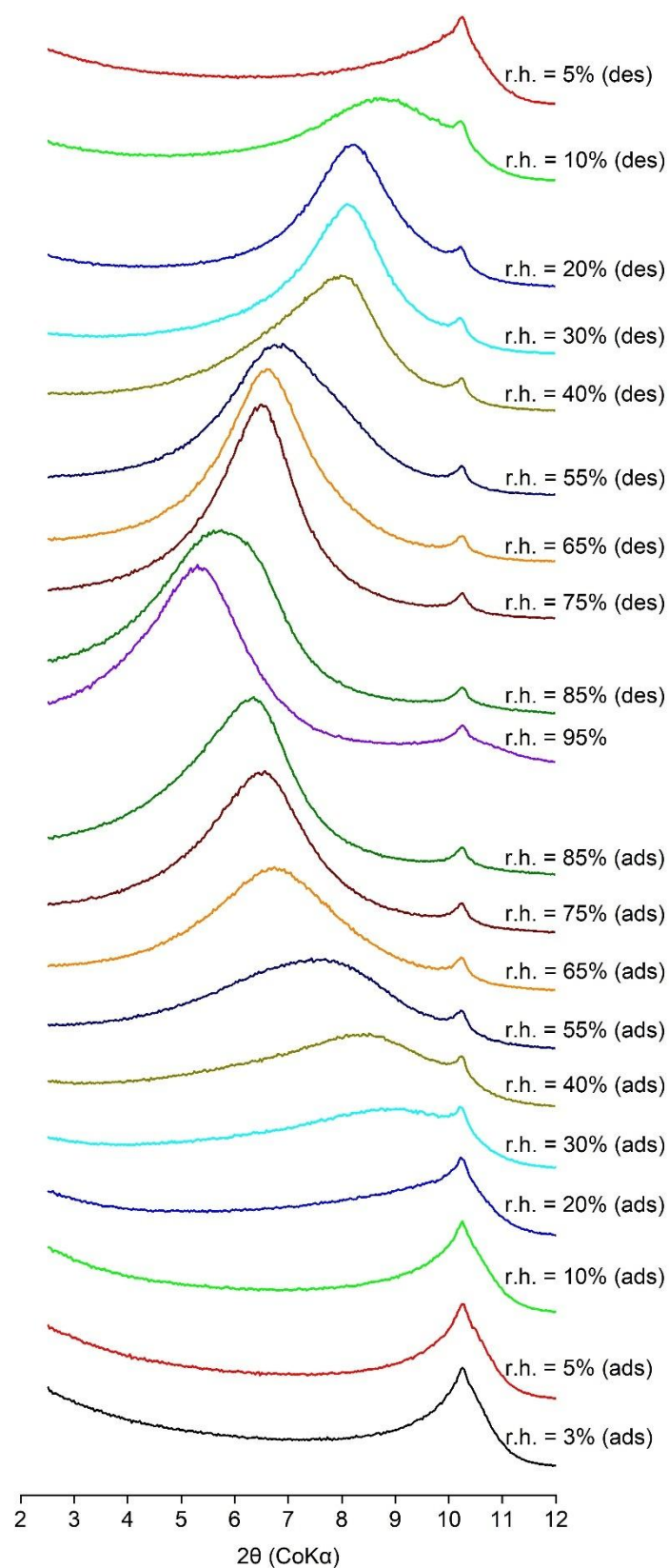


Figure 6.14: XRD isotherm of Calcigel Na⁺-homoionic saturated montmorillonite (Cal_Na)

Comparison of the adsorption and desorption branches reveals pronounced hydration hysteresis. At 10% r.h., d_{001} is approximately 10.0 Å during adsorption but 11.8 Å during desorption. This difference persists at 55% r.h., where the respective values are 13.8 and 14.9 Å, and at 85% r.h., where they reach 16.1 and 17.8 Å. The branches converge at 95% r.h., with both reaching approximately 19.3 Å. This non-coincidence indicates that the interlayer structure depends on the preceding hydration–dehydration pathway. Possible mechanisms include the reorganisation of Na^+ hydration shells, changes in water-molecule arrangements, hydrogen bonding, and kinetic limitations during water uptake and release. These mechanisms are plausible explanations rather than individually proven processes, as the present XRD data cannot quantify their respective contributions (Mooney et al., 1952; Oueslati & Meftah, 2018).

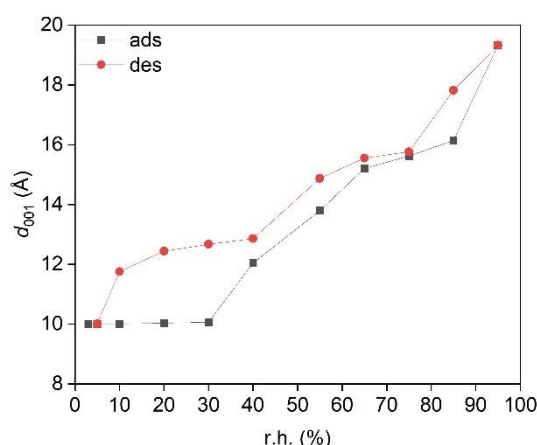


Figure 6.15: d_{001} Calcigel Na^+ -homoionic saturated montmorillonite (Cal_Na) as function of r.h.

Compared with untreated, Ca/Mg-rich Calcigel Raw, which exhibits a low-r.h. basal spacing of approximately 12.3 Å, the Cal_Na sample retains a spacing near 10.0 Å during adsorption up to 30% r.h.. This contrast indicates a different low-humidity hydration response and is consistent with the influence of exchangeable cations on interlayer water organisation. However, attributing the entire difference exclusively to Na^+ substitution requires comparable preparation, equilibration, and measurement conditions. Overall, Cal_Na progresses from predominantly 0W-like hydration at low r.h. through transitional and 2W-dominated regimes to highly hydrated, 3W-like configurations at high r.h.. The observed hysteresis further demonstrates that basal expansion is governed by both ambient humidity and the structural history of the clay–water– Na^+ system.

XRD patterns of Calcigel K^+ - homoionic saturated montmorillonite (Cal_K) exhibit humidity-dependent changes in the basal (001) reflection, indicating interlayer expansion associated with water uptake (Figure 6.16). During adsorption, the basal spacing d_{001} increases from approximately 10.4–10.5 Å at 3–10% r.h. to 10.8 Å at 20% r.h., 11.0–11.2 Å at 30–40% r.h., and 12.1–12.2 Å at 55–65% r.h.. It subsequently reaches approximately 12.4–12.5 Å at 75% r.h. and 12.6 Å at 85–95% r.h.. During desorption, d_{001} increases from approximately 10.5 Å at 5–10% r.h. to 11.0 Å at 30–40% r.h., 11.2 Å at 55% r.h., 11.7 Å at 65% r.h., and 12.1 Å at 75% r.h.. Both branches converge at approximately 12.6 Å at high r.h. (Figure 6.17). Overall, these changes indicate restricted crystalline swelling, with the maximum basal expansion remaining characteristic of a predominantly monohydrated (1W-like) configuration (Ferrage et al., 2005; Morodome & Kawamura, 2011).

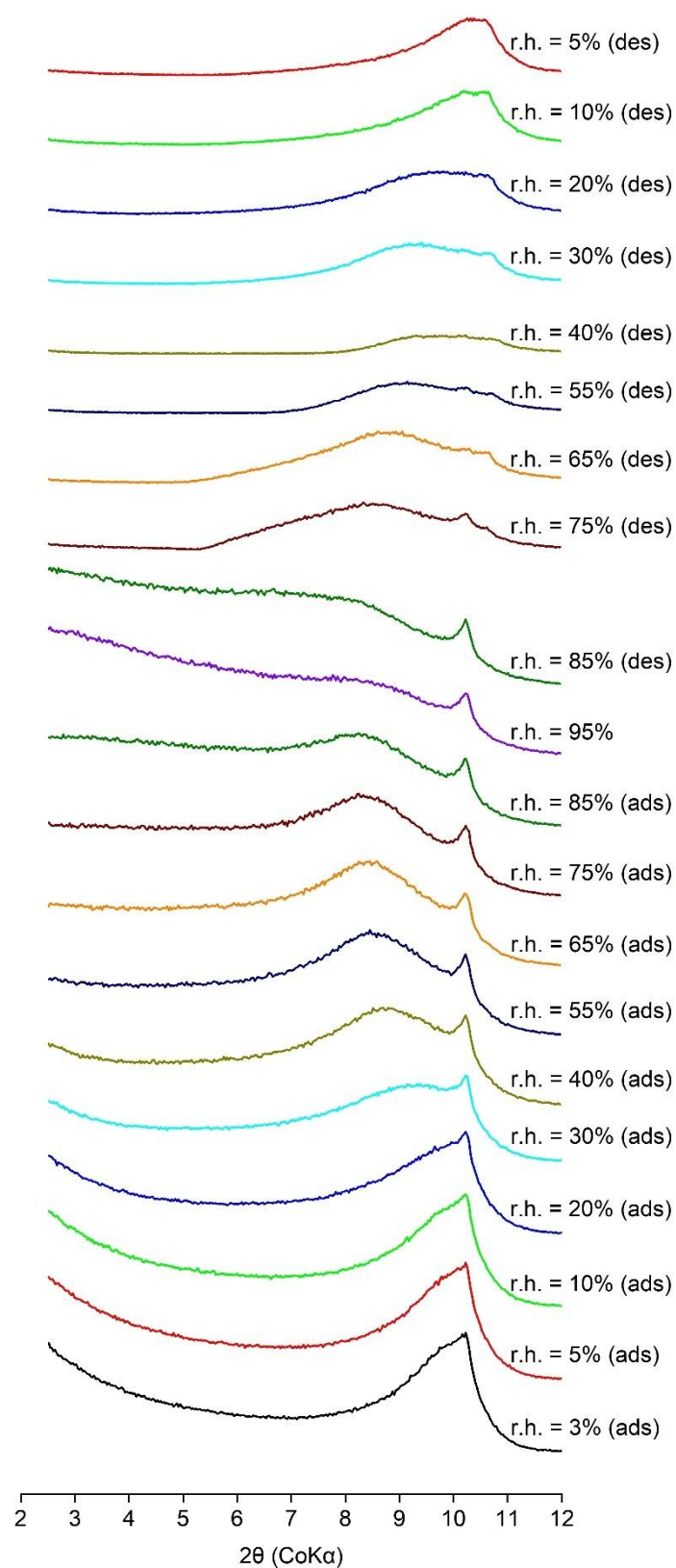


Figure 6.16: XRD isotherm of Calcigel K⁺-homoionic saturated montmorillonite (Cal_K)

At low r.h., basal spacings of approximately 10.4–10.5 Å are consistent with a compact, predominantly zero-water-layer-like (0W-like) configuration, in which no distinct interlayer water layer is established. The gradual increase to 10.8–11.2 Å at 20–40% r.h. suggests progressive hydration towards a 1W-like state. However, these intermediate spacings remain below the approximately 12–12.6 Å range commonly associated with a well-developed 1W configuration. This interval is therefore better interpreted as a transitional hydration regime than as evidence of a uniform hydration state. Variations in water distribution, interlayer cation arrangement, and the coexistence of differently hydrated layers may contribute to the gradual expansion and broadening of the basal reflection (Ferrage et al., 2005).

Between 55% and 75% r.h., adsorption produces basal spacings of approximately 12.1–12.5 Å, whereas desorption yields approximately 11.2–12.1 Å. These values are consistent with the development of a predominantly 1W-like configuration, although their differences indicate a dependence on hydration history. At 85–95% r.h., both branches converge at approximately 12.6 Å, suggesting that basal expansion approaches a plateau. Notably, the spacing does not approach the approximately 15–16 Å range characteristic of a typical 2W configuration or the approximately 18–19 Å range associated with a 3W configuration. Thus, the data provide no clear evidence of dominant 2W or 3W hydration states under the investigated conditions. Nevertheless, confirming a homogeneous 1W structure would require modelling the complete XRD profiles rather than interpreting the maximum (001) reflection alone (Ferrage et al., 2005).

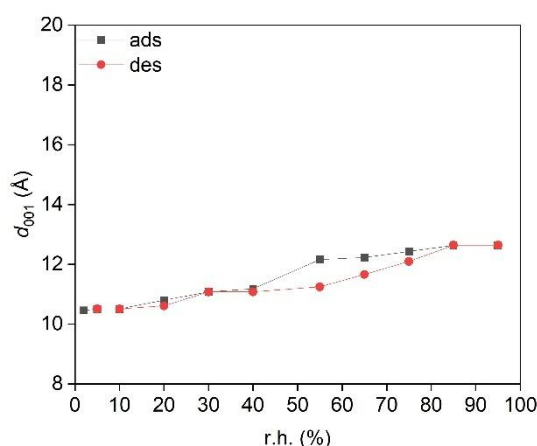


Figure 6.17: d_{001} Calcigel K⁺-homoionic saturated montmorillonite (Cal_K) as function of r.h.

Comparison of the adsorption and desorption branches reveals r.h.-dependent hydration hysteresis. The curves nearly overlap at 5–10% RH, and their differences remain relatively small at 20–40% r.h.. In contrast, adsorption produces greater basal spacings than desorption at 55–75% r.h., with the largest differences occurring at 55–65% r.h.. The branches converge again at 85–95% r.h.. This pattern demonstrates that the direction and magnitude of hysteresis vary with humidity and that the dehydration pathway does not simply retrace the adsorption pathway. The observed differences may reflect water redistribution, reorganisation of interlayer K⁺ ions, cation–surface interactions, and kinetic limitations during hydration and dehydration. Molecular simulations indicate that K⁺ tends to form inner-sphere complexes near basal siloxane surfaces, providing a plausible explanation for restricted swelling and a path-dependent structural response. However, the present XRD data cannot independently establish the relative contributions of these mechanisms (Chávez et al., 2004; Yotsuji et al., 2021).

Comparison with Cal_Na further highlights the influence of exchangeable cations. Whereas the Cal_Na sample expands substantially at high r.h., reaching approximately 19.3 Å, the Cal_K sample remains near 12.6 Å. This contrast is consistent with the stronger association of K⁺ with siloxane surfaces and its lower tendency to promote extensive crystalline swelling relative to Na⁺ under comparable conditions. However, the entire difference cannot be attributed exclusively to cation identity unless sample preparation, r.h. equilibration, and measurement conditions are comparable (Morodome & Kawamura, 2011; Yotsuji et al., 2021).

The diffractograms also contain a comparatively narrow reflection near $2\theta = 10.2^\circ$ that remains relatively stationary as r.h. changes, while the broader basal feature shifts with hydration. For Co-K α radiation, this angular position corresponds to a spacing of approximately 10.1 Å. The stationary reflection may represent a contribution from a relatively non-expandable phase, such as mica or illite, but this assignment remains tentative because a single reflection is insufficient for definitive mineral identification.

In summary, Cal_K exhibits limited basal expansion, from approximately 10.4–10.5 Å at low r.h. to 12.6 Å at high r.h.. The observed changes are consistent with a transition from predominantly 0W-like hydration towards a 1W-dominated regime, without clear evidence of dominant 2W or 3W states. The non-coincidence of the adsorption and desorption branches demonstrates hydration hysteresis, while the restricted expansion is consistent with the influence of K⁺–water–surface interactions.

XRD patterns of Calcigel Ca²⁺- homoionic saturated montmorillonite (Cal_Ca) show a progressive shift of the basal (001) reflection towards lower 2θ values with increasing r.h., indicating interlayer expansion caused by water uptake (Figure 6.18). During adsorption, the basal spacing d_{001} increases from approximately 12.2 Å at 3% r.h. to 14.1 Å at 20% r.h., 15.0–15.3 Å at 30–40% r.h., and 15.8–16.2 Å at 55–75% r.h.. It subsequently reaches 16.7 Å at 85% r.h. and 19.5 Å at 95% r.h.. During desorption, the corresponding spacings are approximately 12.5 Å at 5% r.h., 14.6 Å at 20% r.h., 15.1–15.6 Å at 30–40% r.h., 15.9–16.2 Å at 55–75% r.h., and 17.4 Å at 85% r.h.. Both branches converge at approximately 19.5 Å at 95% r.h. (Figure 6.19) These changes demonstrate progressive hydration and crystalline swelling of the smectitic component (Ferrage et al., 2005; Morodome & Kawamura, 2011).

At low r.h., basal spacings of approximately 12.2–13.2 Å are consistent with a predominantly monohydrated (1W-like) configuration rather than a fully dehydrated zero-water-layer (0W) state, typically associated with spacings of approximately 9.6–10.2 Å. This behaviour indicates that interlayer water remains associated with the Ca-saturated clay under relatively dry conditions. The strong hydration affinity of Ca²⁺ provides a plausible explanation, although the present XRD data cannot directly determine the cation coordination environment (Ferrage et al., 2005; Wang et al., 2025).

At approximately 20–30% r.h., d_{001} increases to 14.1–15.1 Å, indicating a transition from predominantly 1W-like towards bihydrated (2W-like) configurations. This interval should be regarded as a transitional regime rather than a uniform hydration state, because interlayers with different hydration states may coexist. Between 30% and 75% r.h., basal spacings of approximately 15.0–16.2 Å indicate a predominantly 2W-like regime. The gradual expansion towards 16.2 Å suggests continued structural adjustment involving water distribution, Ca²⁺ hydration, and interlayer thickness, rather than an abrupt transition to an additional complete water layer (Ferrage et al., 2005, 2007a).

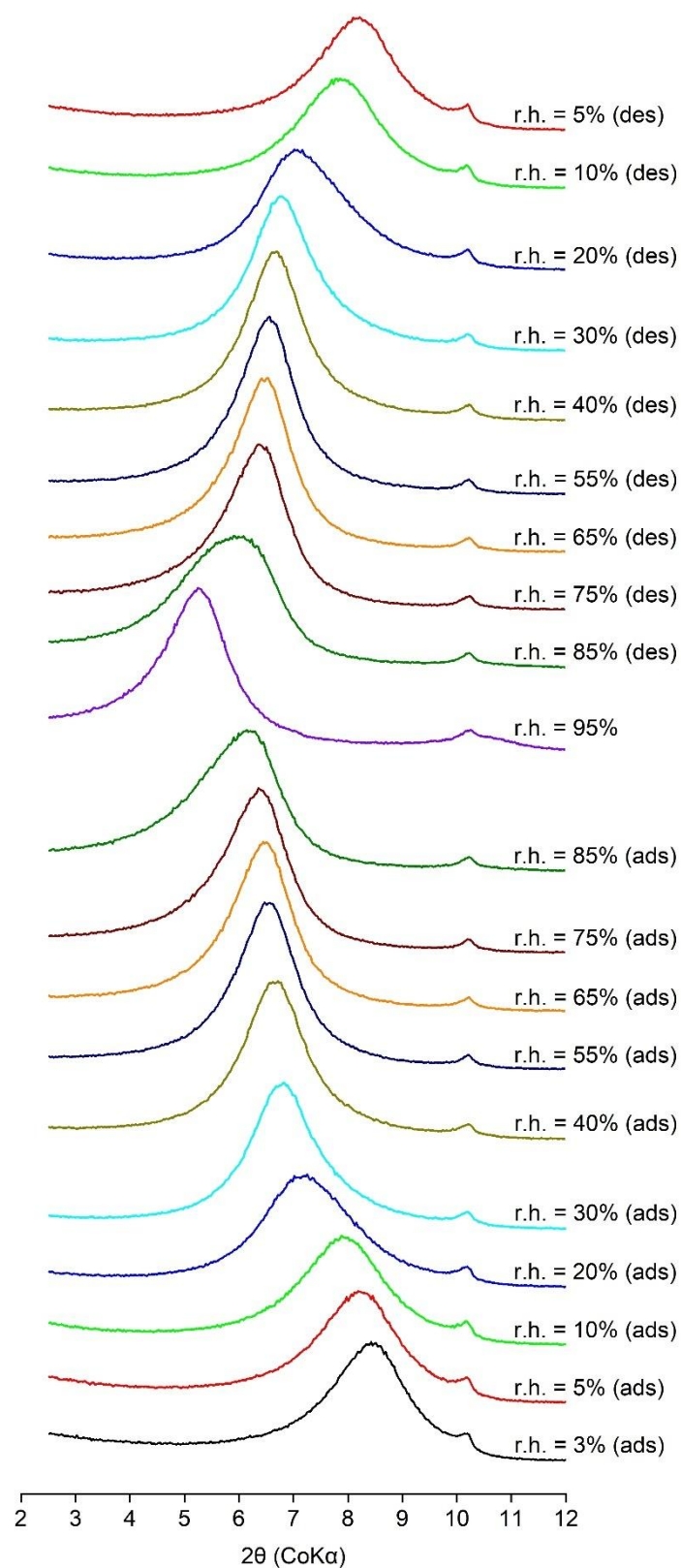


Figure 6.18: XRD isotherm of Calcigel Ca²⁺-homoionic saturated montmorillonite (CaI_Ca)

At 85% r.h., the basal spacing reaches approximately 16.7 Å during adsorption and 17.4 Å during desorption, suggesting a transition towards more highly hydrated configurations. At 95% r.h., both branches reach approximately 19.5 Å, consistent with extensive hydration and a 3W-like configuration. However, this value slightly exceeds the commonly reported 18–19 Å range for an idealised 3W state and does not establish a homogeneous three-water-layer structure. The most defensible interpretation is therefore a progression from predominantly 1W-like hydration at low r.h., through a 1W–2W transition and a 2W-dominated regime, towards 3W-like hydration at high r.h.. Confirming the proportions of these states requires modelling the complete XRD profiles (Ferrage et al., 2005, 2007a, 2007b).

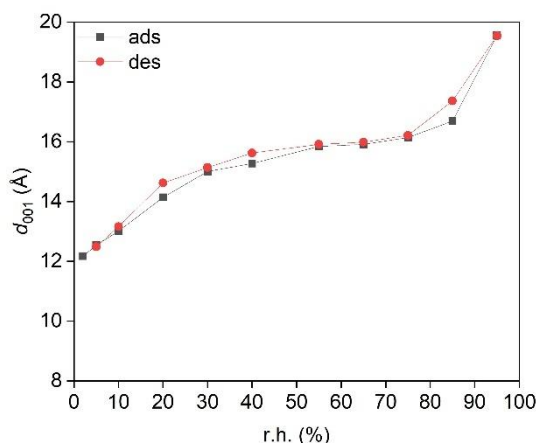


Figure 6.19: d_{001} Calcigel Ca^{2+} -homoionic saturated montmorillonite (Cal_Ca) as function of r.h.

Comparison of the adsorption and desorption branches reveals hydration hysteresis. At 20% r.h., d_{001} is approximately 14.1 Å during adsorption and 14.6 Å during desorption; at 40% r.h., the corresponding values are approximately 15.3 and 15.6 Å. The difference becomes more pronounced at 85% r.h., reaching 16.7 Å during adsorption and 17.4 Å during desorption, before the branches converge at 19.5 Å at 95% r.h.. This non-coincidence demonstrates that the basal structure depends on the preceding hydration–dehydration pathway. Possible mechanisms include changes in Ca^{2+} hydration shells, interlayer water organisation, hydrogen bonding, and kinetic limitations during water uptake and release. Molecular simulations support the plausibility of these mechanisms, but their individual contributions cannot be established from the present XRD data alone (Fu et al., 1990; Wang et al., 2025).

Comparison with Cal_K further highlights the influence of exchangeable cations. Whereas the Cal_Ca sample expands to approximately 19.5 Å at 95% r.h., the Cal_K sample remains near 12.6 Å. This contrast is consistent with the stronger restriction of crystalline swelling by K^+ relative to Ca^{2+} under the investigated conditions. Nevertheless, attributing the entire difference to cation identity requires comparable sample preparation, cation-exchange efficiency, and r.h. equilibration conditions. Overall, the Cal_Ca sample exhibits substantial humidity-dependent swelling and a path-dependent structural response, consistent with the coupled effects of water activity, interlayer cation hydration, and interlayer organisation.

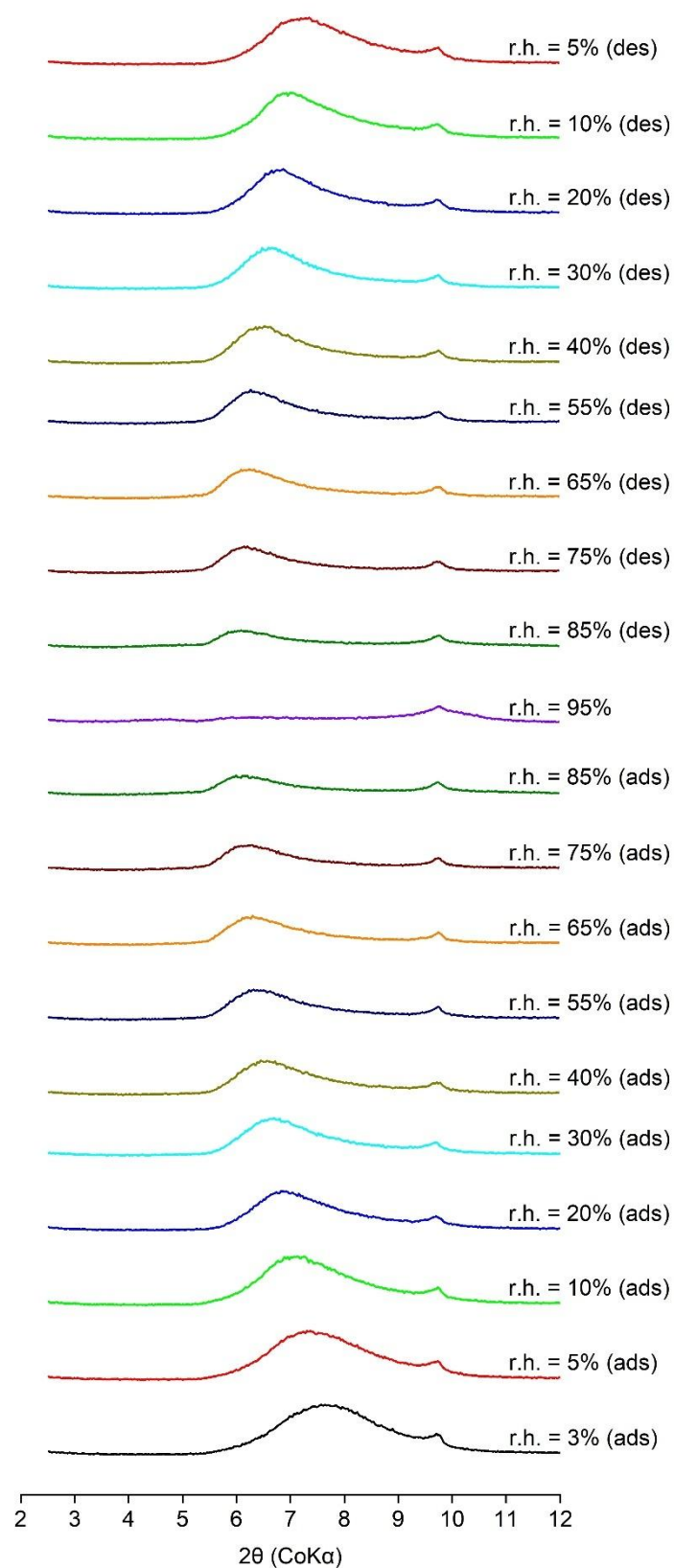


Figure 6.20: XRD isotherm of Calcigel Mg^{2+} -homoionic saturated montmorillonite (CaI_Mg)

XRD patterns of Calcigel Mg^{2+} - homoionic saturated montmorillonite (Cal_Mg) show progressive changes in the basal (001) reflection with increasing r.h., indicating interlayer expansion associated with water uptake (Figure 6.20). During adsorption, the basal spacing d_{001} increases from approximately 13.4 Å at 3% r.h. to 14.4 Å at 10% r.h., 15.0 Å at 20–30% r.h., and 15.9 Å at 40% r.h.. It subsequently reaches approximately 16.4–16.5 Å at 55% r.h., decreases slightly to 16.3–16.4 Å at 65–75% r.h., and increases to 17.1 Å at 85% r.h.. During desorption, the basal spacing is generally greater at intermediate and high RH, reaching approximately 16.6 Å at 55% r.h. and 16.8–16.9 Å at 65–75% r.h., before approaching 17.1 Å at 85% r.h. (Figure 6.21). These changes indicate progressive interlayer hydration and crystalline swelling, influenced by both water activity and hydration history (Ferrage et al., 2005; Sun & Tsukahara, 2020).

At low r.h., basal spacings of approximately 13.4–14.4 Å lie between typical monohydrated (1W) and bihydrated (2W) configurations. These values are better interpreted as apparent spacings associated with transitional or heterogeneous hydration than as evidence of a uniform hydration state. The strong hydration affinity of Mg^{2+} can influence interlayer-water organisation even at relatively low humidity. Consequently, the observed spacing alone cannot establish the proportions of individual hydration states throughout the crystallites (Ferrage et al., 2005; Sun & Tsukahara, 2020).

Between 20% and 40% r.h., d_{001} increases from approximately 15.0 to 15.9 Å, indicating the development of a predominantly 2W-like hydration regime. The continued expansion towards 16 Å suggests that the interlayer structure remains responsive to increasing humidity. Between 55% and 75% r.h., the spacing ranges from approximately 16.3 to 16.9 Å, with a slight decrease during adsorption but generally higher values during desorption. This behaviour may reflect changes in water distribution, interlayer thickness, and the coexistence of differently hydrated layers rather than a simple increase in the number of complete water layers. XRD profile modelling has demonstrated that smectite crystallites commonly contain interlayers with different hydration states, particularly during hydration transitions (Ferrage et al., 2005).

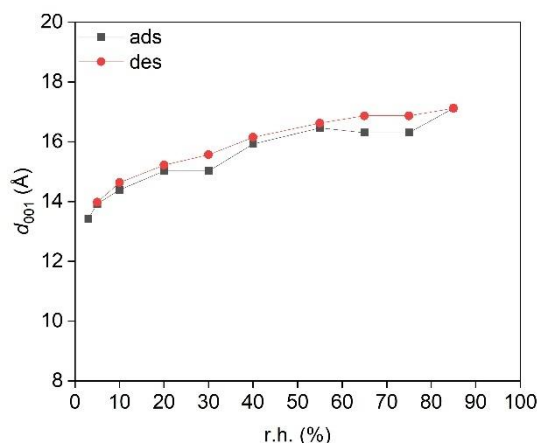


Figure 6.21: d_{001} Calcigel Mg^{2+} -homoionic saturated montmorillonite (Cal_Mg) as function of r.h.

At 85% r.h., the basal spacing approaches 17.1 Å in both branches, although the plotted values indicate a small difference between adsorption and desorption. This spacing lies between the typical ranges associated with 2W and trihydrated (3W) configurations and is therefore more appropriately interpreted as an intermediate, highly hydrated structure than as definitive evidence of a homogeneous 3W phase. The diffractogram labelled 95% r.h. requires particular caution: its basal

reflection is weak and diffuse, making its maximum difficult to determine reliably. Although the d_{001} -r.h. plot appears to include a value near 17.1 Å for the final desorption point, that value should be treated as provisional because the corresponding reflection is not clearly resolved. The available data therefore do not establish a reliable basal spacing or confirm a 3W state at 95% r.h..

Comparison of the adsorption and desorption branches reveals humidity-dependent structural hysteresis. At 55% r.h., the difference is small, with spacings of approximately 16.4–16.5 Å during adsorption and 16.6 Å during desorption. At 65–75% r.h., the desorption values exceed the adsorption values by approximately 0.5–0.6 Å. The difference becomes less evident at 85% r.h., where the branches approach 17.1 Å. This non-coincidence indicates that the interlayer structure does not follow an entirely reversible hydration–dehydration pathway. Possible mechanisms include the reorganisation of Mg^{2+} hydration shells, changes in water-molecule distribution, hydrogen bonding, and kinetic limitations during water uptake and release. These explanations are consistent with established studies of cation-dependent interlayer hydration, although the individual mechanisms cannot be distinguished using the present XRD data alone (Fu et al., 1990; Sun & Tsukahara, 2020).

Cal_Mg exhibits an increase in apparent basal spacing from approximately 13.4 Å at low r.h. to 17.1 Å at 85% r.h.. The results indicate a transition from heterogeneous 1W–2W-like configurations towards predominantly 2W-like hydration at intermediate r.h. and more highly hydrated structures at high r.h.. The weak, diffuse reflection at 95% RH prevents reliable assignment of its basal spacing or hydration state. The most pronounced hysteresis occurs at 65–75% RH, where desorption spacings exceed adsorption values by approximately 0.5–0.6 Å. These findings demonstrate that interlayer hydration depends on water activity, Mg^{2+} –water interactions, hydration-state heterogeneity, and the preceding hydration history. Quantitative identification of individual hydration states requires modelling the complete XRD profiles rather than relying solely on the maximum of the (001) reflection.

XRD patterns of Secursol UHP Raw (Sec_R) show a shift of the montmorillonite basal (001) reflection towards lower 2θ values as r.h. increases, indicating interlayer expansion caused by water uptake (Figure 6.22). During adsorption, the basal spacing d_{001} increases from approximately 12.2–12.3 Å at 3–5% r.h. to 12.9 Å at 10% r.h., 14.4 Å at 20% r.h., and 15.0–15.8 Å at 30–75% r.h.. It subsequently reaches 16.1 Å at 85% r.h. and 19.1 Å at 95% r.h.. During desorption, the corresponding values increase from approximately 12.6 Å at 5% r.h. to 13.5 Å at 10% r.h., 14.6 Å at 20% r.h., and 15.1–16.0 Å at 30–75% r.h., before reaching 17.1 Å at 85% r.h. and 19.1 Å at 95% r.h. (Figure 6.23). These trends demonstrate progressive interlayer hydration and crystalline swelling, accompanied by differences between the adsorption and desorption pathways (Ferrage et al., 2005; Ferrage et al., 2007a).

At low r.h., basal spacings of approximately 12.2–13.5 Å are consistent with predominantly monohydrated (1W-like) configurations or transitional hydration towards bihydrated (2W-like) layers, rather than a dehydrated zero-water-layer (0W) state, typically characterised by spacings of approximately 9.6–10.2 Å. This behaviour suggests that the smectitic component retains interlayer water under relatively dry conditions. Hydration of exchangeable Ca^{2+} and Mg^{2+} ions may contribute to this response; however, basal spacing alone cannot establish their local coordination environments or confirm a uniform hydration state throughout the sample (Ferrage et al., 2005).

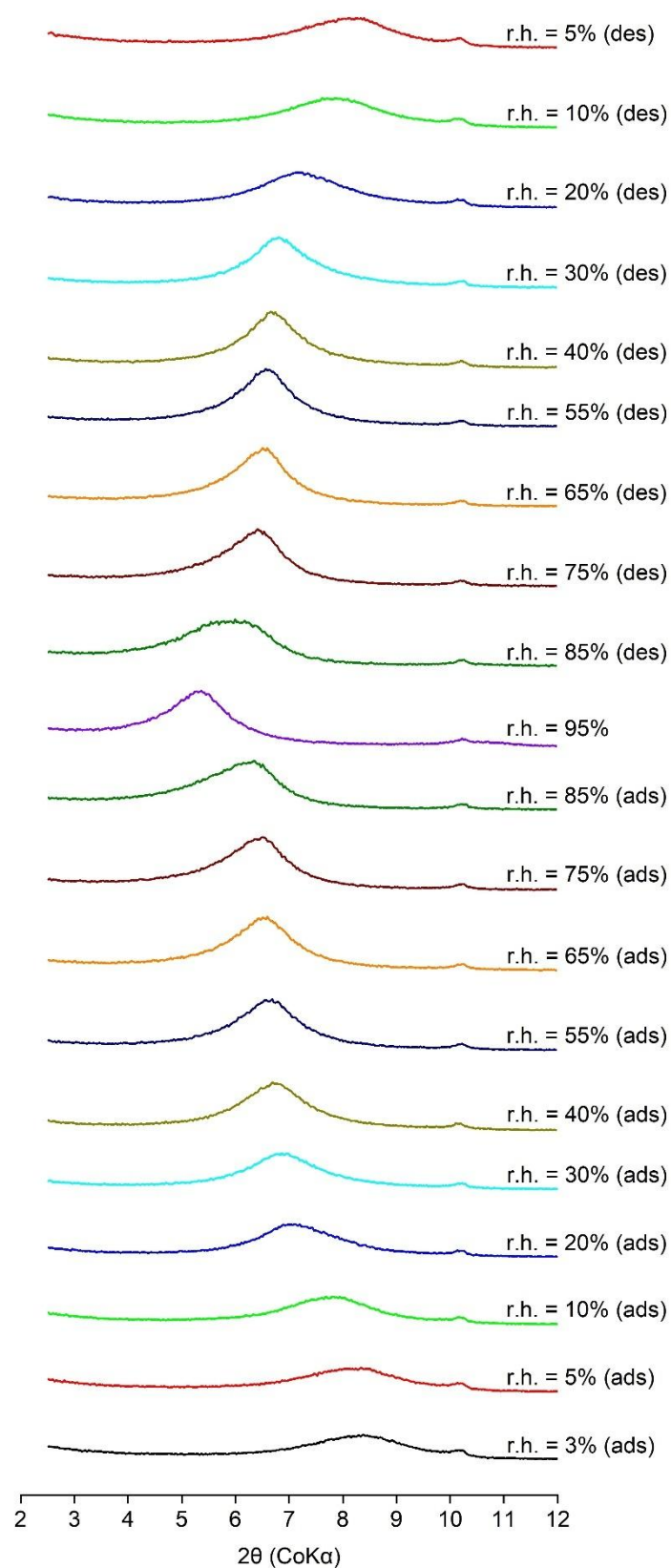


Figure 6.22: XRD isotherm of Secursol UHP Raw (Sec_R)

Between 10% and 20% r.h., d_{001} increases to approximately 14.4–14.6 Å, indicating a transition towards 2W-dominated hydration. At 20–75% r.h., spacings of approximately 14.4–16.0 Å suggest progressive development of a predominantly 2W-like regime. The gradual expansion towards 15.8–16.0 Å does not necessarily indicate the formation of a dominant 3W state; it may instead reflect variations in interlayer thickness, water distribution, and the proportions of coexisting hydration states. Such heterogeneity is consistent with XRD studies showing that smectite crystallites can contain layers with different hydration states simultaneously (Ferrage et al., 2005, 2007a).

At 85% r.h., the basal spacing reaches approximately 16.1 Å during adsorption and 17.1 Å during desorption, a difference of about 1.0 Å. Both values remain below the typical 18–19 Å range associated with a 3W configuration and are therefore better interpreted as transitional structures approaching higher hydration. At 95% r.h., the two branches converge at approximately 19.1 Å, consistent with extensive hydration and a 3W-like configuration. This sequence represents the dominant hydration behaviour rather than proof that every interlayer adopts an identical structure. Quantitative determination of the proportions of 1W, 2W, and 3W layers requires modelling the complete XRD profiles (Ferrage et al., 2005, 2007a).

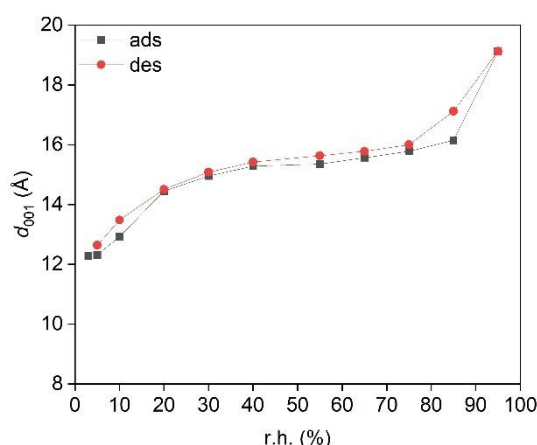


Figure 6.23: d_{001} Secursol UHP Raw (Sec_R) as function of r.h.

The divergence between the adsorption and desorption branches demonstrates hydration hysteresis. Differences are relatively small at low and intermediate r.h. but become most pronounced at 85% r.h., where the desorption spacing exceeds the adsorption value by approximately 1.0 Å. Their convergence at 95% RH indicates that the structural difference becomes less evident under very humid conditions. This path dependence may involve changes in interlayer-water organisation, cation hydration, layer stacking, and kinetic limitations during water uptake and release. Nevertheless, the present XRD data cannot independently establish the relative contributions of these mechanisms (Ferrage et al., 2007a, 2007b).

The hydration response must also be considered in the context of the bentonite's mineralogical composition and inherited fabric. Secursol UHP contains approximately 79% dioctahedral smectite, identified as montmorillonitic–beidellitic smectite with significant octahedral iron. Its smectite has a slightly higher layer charge and broader particle-size distribution than that of Calcigel. Despite its higher smectite content, Secursol UHP exhibits lower water uptake and poorer dispersibility in deionised water, attributed to its inherited fabric restricting expansion (Asaad et al., 2025). Consequently, its humidity-dependent basal expansion reflects not only interlayer hydration but also

the combined effects of exchangeable cations, layer charge, crystallite stacking, and aggregate structure.

Sec_R progresses from predominantly 1W-like hydration at low r.h. towards a 2W-dominated regime at intermediate r.h. and a highly hydrated, 3W-like configuration at 95% r.h.. The pronounced difference between adsorption and desorption at 85% r.h. demonstrates a path-dependent structural response. These findings highlight the combined influence of interlayer-water organisation, exchangeable-cation hydration, hydration-state heterogeneity, and inherited fabric on the crystalline swelling of natural bentonite.

XRD patterns of Secursol UHP Na⁺- homoionic saturated montmorillonite (Sec_Na) show humidity-dependent shifts of the basal (001) reflection towards lower 2 θ values, indicating interlayer expansion during water uptake (Figure 6.24). During adsorption, the basal spacing d_{001} remains approximately 10.0 Å between 5% and 20% r.h., before increasing to 11.9 Å at 30% r.h., 12.3 Å at 40% r.h., 12.8 Å at 55% r.h., and 14.7 Å at 65% r.h.. It subsequently reaches 15.3 Å at 75% r.h., 16.0 Å at 85% r.h., and 17.9 Å at 95% r.h.. During desorption, d_{001} increases from approximately 10.0 Å at 5% RH to 12.2–12.9 Å at 10–40% r.h., 14.7 Å at 55% r.h., 15.2–15.7 Å at 65–75% r.h., and 16.4 Å at 85% r.h.. Both branches converge at approximately 17.9 Å at 95% r.h., (Figure 6.25) demonstrating progressive hydration and a path-dependent structural response (Ferrage et al., 2005; Oueslati & Meftah, 2018).

The persistence of a basal spacing near 10.0 Å during adsorption up to 20% RH is consistent with a predominantly zero-water-layer (0W-like) configuration. Expansion becomes evident at 30% r.h., where d_{001} reaches 11.9 Å, and continues towards a monohydrated (1W-like) configuration at 30–55% r.h.. In contrast, desorption produces spacings of 12.2–12.9 Å at 10–40% r.h., indicating that expanded interlayers persist after exposure to higher humidity. The transition from 0W-like to 1W-like hydration is therefore pathway-dependent rather than governed by a single r.h. threshold. Moreover, the maximum (001) reflection cannot establish that all interlayers share the same hydration state, as different layer types may coexist within smectite crystallites (Ferrage et al., 2005).

A pronounced expansion occurs between 55% and 65% r.h. during adsorption, with d_{001} increasing from 12.8 to 14.7 Å, consistent with a transition towards a bihydrated (2W-like) configuration. At 75–85% r.h, spacings of 15.3–16.0 Å indicate predominantly 2W-like hydration, potentially accompanied by heterogeneous interlayer expansion. During desorption, the corresponding spacings increase from 14.7 Å at 55% r.h. to 16.4 Å at 85% r.h., suggesting that more expanded configurations persist at comparable humidity. At 95% r.h., the spacing reaches 17.9 Å in both branches, consistent with extensive hydration approaching a trihydrated (3W-like) configuration. However, this value alone does not demonstrate a homogeneous 3W structure; confirming the relative proportions of 0W, 1W, 2W, and 3W layers requires modelling the complete XRD profiles (Ferrage et al., 2005; Oueslati & Meftah, 2018).

The adsorption and desorption branches exhibit pronounced hydration hysteresis. The largest difference occurs at 20% r.h., where d_{001} is approximately 10.0 Å during adsorption and 12.5 Å during desorption, a difference of about 2.5 Å. At 55% r.h., the corresponding values are 12.8 and 14.7 Å, respectively, giving a difference of approximately 1.9 Å. This discrepancy decreases to approximately 0.4–0.5 Å at 65–85% r.h., before the branches converge at 17.9 Å at 95% r.h.. These differences indicate that hydration and dehydration follow distinct structural pathways. Possible mechanisms include the reorganisation of interlayer Na⁺ ions and water molecules, changes in hydrogen bonding, and kinetic limitations during water uptake and release. Although these mechanisms are plausible, their individual contributions cannot be established from the present XRD data alone (Fu et al., 1990; Oueslati & Meftah, 2018).

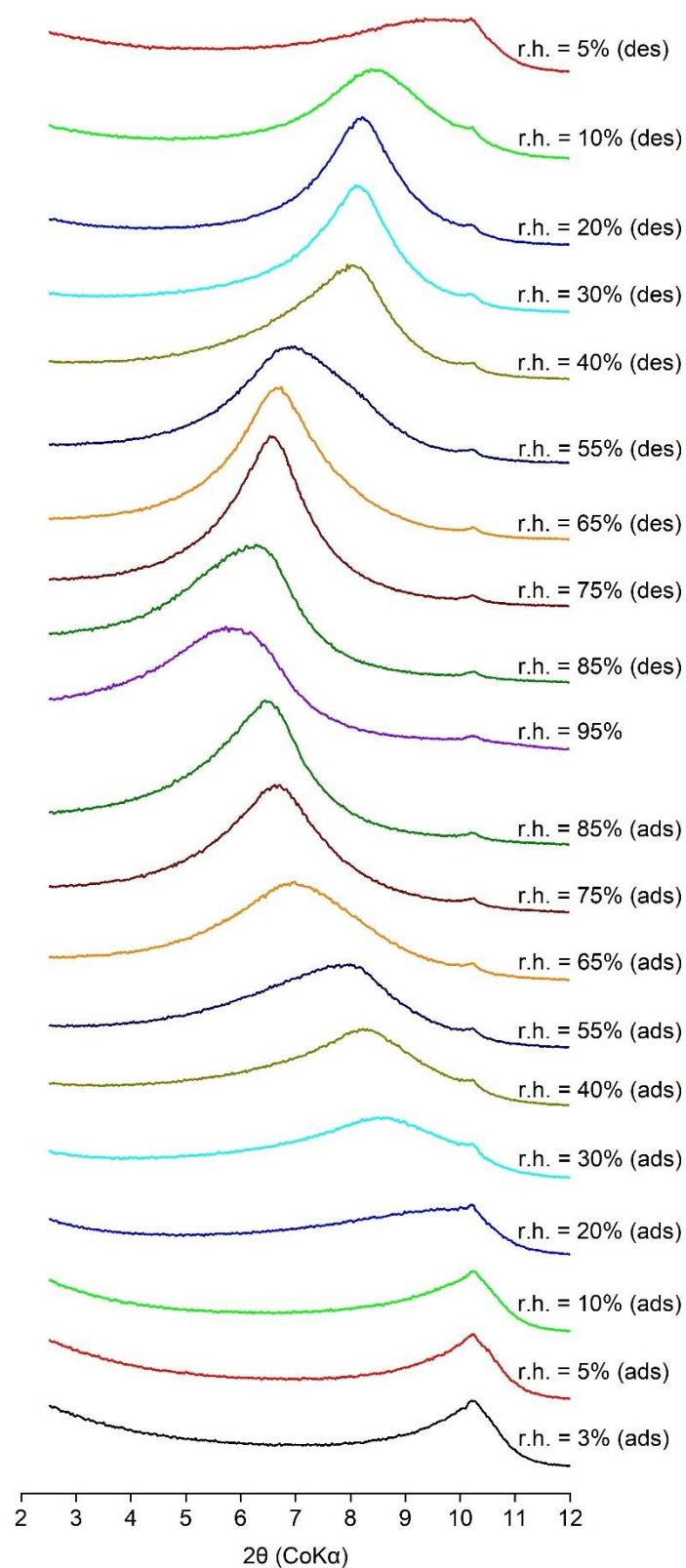


Figure 6.24: XRD isotherm of Secursol UHP Na⁺-homoionic saturated montmorillonite (Sec_Na)

The comparison with Cal_Na highlights the influence of the bentonite's intrinsic properties on hydration. Secursol UHP retains a 0W-like spacing until approximately 20% r.h. during adsorption, whereas Calcigel begins expanding at a higher r.h. in the previously examined dataset. At 95% r.h., however, both samples reach highly expanded structures, with basal spacings of approximately 17.9 Å for Secursol UHP and 19.3 Å for Calcigel. Mineralogical characterisation shows that Secursol UHP contains approximately 79% dioctahedral smectite, compared with 61% in Calcigel. Despite its higher smectite content, Secursol UHP exhibits lower water uptake and poorer dispersibility in deionised water, attributed to its inherited fabric restricting expansion. Differences in layer charge, particle-size distribution, average basal surface, and crystallite stacking may therefore contribute to the contrasting hydration responses (Asaad et al., 2025).

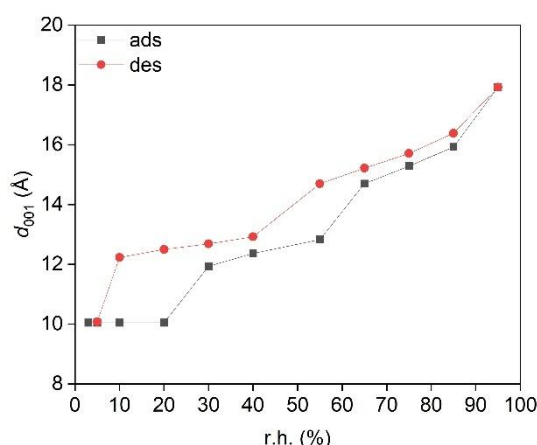


Figure 6.25: d_{001} Secursol UHP Na⁺-homoionic saturated montmorillonite (Sec_Na) as function of r.h.

Sec_Na progresses from predominantly 0W-like hydration at low r.h. through 1W-like and 2W-dominated regimes to a highly hydrated, 3W-like configuration at 95% r.h.. The substantial hysteresis at 20% and 55% r.h. demonstrates that the basal structure depends on the preceding hydration–dehydration pathway as well as the prevailing r.h.. Its hydration behaviour reflects the combined effects of interlayer-water organisation, exchangeable-cation interactions, hydration-state heterogeneity, and inherited mineral fabric. Quantitative identification of the individual hydration states requires modelling of the complete XRD profiles rather than relying solely on the position of the maximum basal reflection.

XRD patterns of Secursol UHP K⁺- homoionic saturated montmorillonite (Sec_K) show humidity-dependent changes in the basal (001) reflection, indicating interlayer expansion associated with water uptake (Figure 6.26). During adsorption, the basal spacing d_{001} remains approximately 10.3–10.5 Å between 3% and 20% r.h., before increasing to 11.2 Å at 30% r.h., 12.0 Å at 40% r.h., and 12.2–12.7 Å at 55–95% r.h.. During desorption, d_{001} increases from approximately 10.4–10.5 Å at 5–10% r.h. to 11.8 Å at 20–30% r.h., 12.1–12.3 Å at 40–55% r.h., and 12.5–12.7 Å at 65–95% r.h. (Figure 6.27). These results indicate limited basal expansion and a structural response influenced by both humidity and hydration history (Ferrage et al., 2005; Yotsuji et al., 2021).

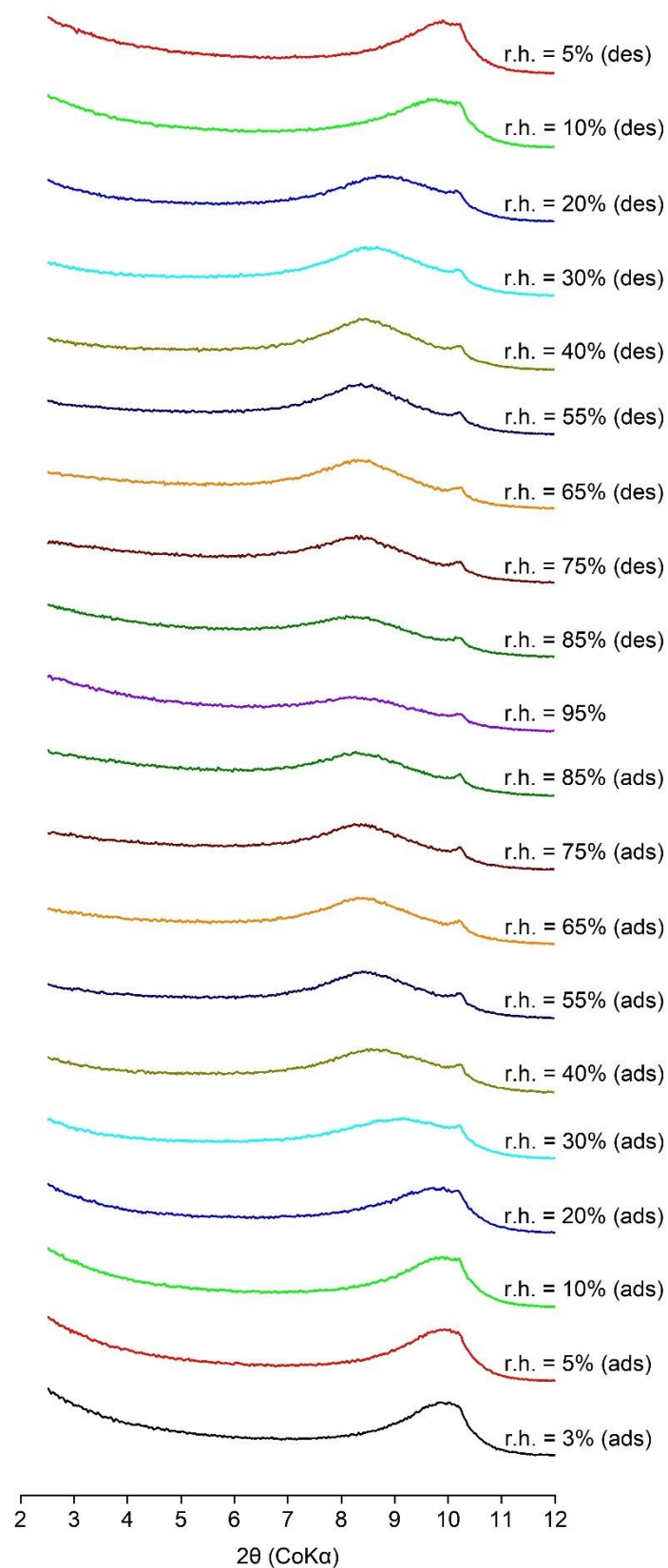


Figure 6.26: XRD isotherm of Secursol UHP K⁺-homoionic saturated montmorillonite (Sec_K)

At low r.h., the adsorption spacing of approximately 10.3–10.5 Å is consistent with a predominantly zero-water-layer (0W-like) configuration. This assignment is indicative rather than definitive, as the values slightly exceed the typical spacing of approximately 9.6–10.2 Å for dehydrated smectite. The compact structure persists until approximately 20% r.h., whereas expansion becomes more apparent at 30–40% r.h., suggesting a transition towards a monohydrated (1W-like) configuration. In contrast, desorption produces a spacing of approximately 11.8 Å at 20% r.h., indicating that a more expanded structure persists at lower humidity following prior hydration. This difference demonstrates that the interlayer structure depends on the hydration pathway, while the maximum (001) reflection alone cannot establish a uniform hydration state throughout the crystallites (Ferrage et al., 2005).

Between 40% and 95% r.h., the adsorption spacing increases gradually from approximately 12.0 to 12.7 Å, while desorption reaches approximately 12.4–12.7 Å. These values are consistent with a predominantly 1W-like hydration regime. Notably, the basal spacing does not approach the approximately 14.6–16.0 Å range commonly associated with a bihydrated (2W) configuration. Thus, the available data provide no compelling evidence that 2W becomes the dominant state, even at 95% r.h.. This restricted swelling is consistent with the behaviour of K-montmorillonite, in which K⁺ ions preferentially associate with basal siloxane surfaces and can form inner-sphere complexes, limiting interlayer expansion (Chávez et al., 2004; Yotsuji et al., 2021). Nevertheless, broad basal reflections may indicate structural heterogeneity, and the coexistence of different hydration states cannot be excluded without modelling the complete XRD profiles.

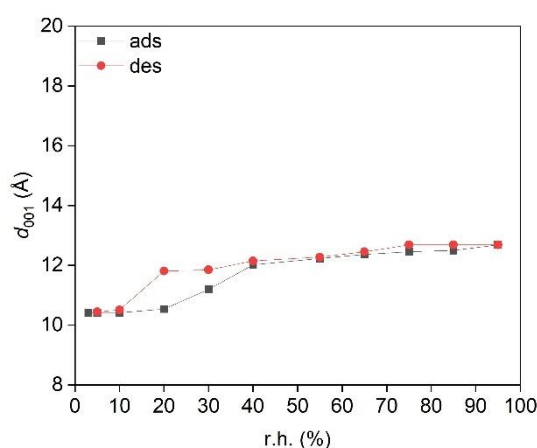


Figure 6.27: d_{001} Secursol UHP K⁺-homoionic saturated montmorillonite (Sec_K) as function of r.h.

Comparison of the adsorption and desorption branches reveals pronounced hysteresis at low to intermediate r.h.. At 20% RH, d_{001} is approximately 10.5 Å during adsorption and 11.8 Å during desorption, giving a difference of approximately 1.3 Å. This difference decreases to approximately 0.6 Å at 30% r.h. and becomes smaller at higher humidity. The branches ultimately converge at approximately 12.7 Å at 95% r.h.. This behaviour indicates that the interlayer structure follows different hydration and dehydration pathways. The hysteresis may reflect changes in interlayer accessibility, water-molecule organisation, and K⁺–surface interactions, although their individual contributions cannot be determined from the present XRD data alone (Chávez et al., 2004; Yotsuji et al., 2021).

Comparison with Sec_Na further highlights the influence of exchangeable cations. Whereas the Sec_Na sample expands to approximately 17.9 Å at 95% r.h., the Sec_K sample reaches only

approximately 12.7 Å. This contrast is consistent with the stronger restriction of crystalline swelling by K^+ than by Na^+ under the investigated conditions. However, the hydration behaviour also reflects the intrinsic mineralogical and microstructural characteristics of the parent bentonite. Secursol UHP contains approximately 79% dioctahedral smectite and exhibits a slightly higher layer charge and broader particle-size distribution than Calcigel. Despite its higher smectite content, Secursol UHP shows lower water uptake and poorer dispersibility in deionised water, attributed to its inherited fabric restricting expansion (Asaad et al., 2025). Consequently, the observed hydration response reflects the combined effects of exchangeable-cation identity, layer charge, crystallite stacking, and aggregate structure.

Sec_K exhibits a transition from predominantly 0W-like hydration at low r.h. towards a 1W-dominated regime, with expansion becoming evident between approximately 20% and 40% r.h.. No compelling evidence indicates that 2W becomes the dominant hydration state up to 95% RH. The pronounced hysteresis at low to intermediate humidity demonstrates that basal expansion depends on the preceding hydration–dehydration pathway. These findings are consistent with the combined influence of K^+ –water–surface interactions and the inherited microstructure of the montmorillonite.

XRD patterns of Secursol UHP Ca^{2+} - homoionic saturated montmorillonite (Sec_Ca) show a shift of the basal (001) reflection towards lower 2θ values as r.h. increases, indicating interlayer expansion due to water uptake (Figure 6.28). During adsorption, the basal spacing d_{001} increases from approximately 12.3–12.9 Å at 3–10% r.h. to 14.5–15.0 Å at 20–30% r.h. and 15.0–15.6 Å at 30–65% r.h.. It subsequently reaches approximately 15.8 Å at 75% r.h., 16.1 Å at 85% r.h., and 19.0 Å at 95% r.h.. During desorption, the spacing increases from approximately 12.5–12.9 Å at 5–10% r.h. to 14.6–15.4 Å at 20–40% r.h., 15.6–16.1 Å at 55–75% r.h., and 17.3 Å at 85% r.h. (Figure 6.29). Both branches converge at approximately 19.0 Å at 95% r.h., demonstrating progressive hydration and a path-dependent structural response (Ferrage et al., 2005, 2007a).

At low r.h., basal spacings of approximately 12.3–12.9 Å are consistent with predominantly monohydrated (1W-like) configurations rather than a fully dehydrated zero-water-layer (0W) state. Interlayer water may be retained through interactions among Ca^{2+} ions, water molecules, and negatively charged clay surfaces. As r.h. increases to 20–30%, d_{001} reaches approximately 14.5–15.0 Å, indicating a transition towards bihydrated (2W-like) configurations. This interval should be interpreted as a transitional regime rather than a homogeneous hydration state, since layers with different hydration states may coexist within individual crystallites. Consequently, the maximum (001) reflection indicates the overall structural response but cannot independently quantify the proportions of 1W and 2W layers (Ferrage et al., 2005).

Between 30% and 65% r.h., basal spacings of approximately 15.0–15.6 Å indicate a predominantly 2W-like regime. The gradual expansion suggests continuing changes in interlayer thickness, water-molecule organisation, and Ca^{2+} hydration shells. At 75–85% r.h., adsorption produces spacings of approximately 15.8–16.1 Å, whereas desorption reaches 16.1 and 17.3 Å, respectively. The desorption value at 85% r.h.. Therefore, indicates a transition towards more highly hydrated configurations, potentially involving coexisting 2W and 3W layers. However, the broad basal reflection does not establish their relative proportions (Ferrage et al., 2005, 2007a).

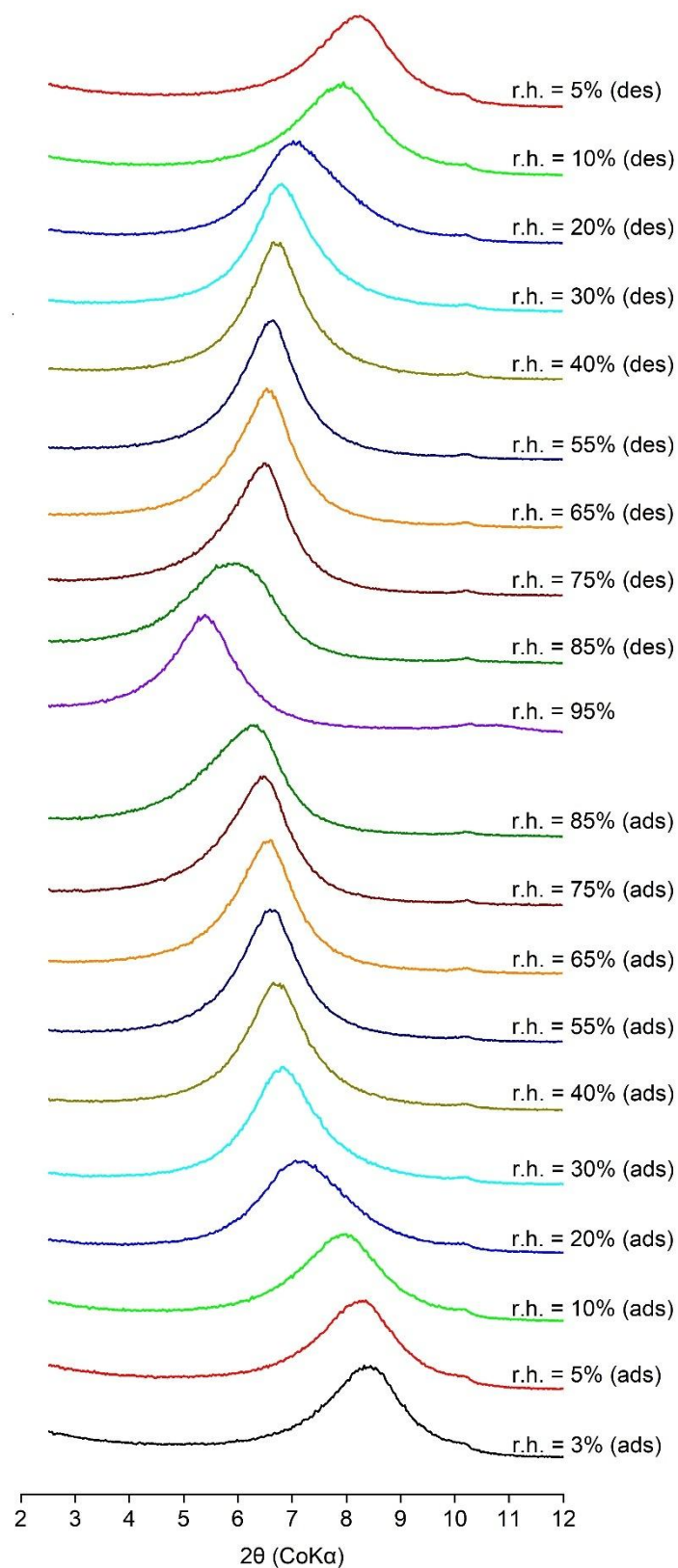


Figure 6.28: XRD isotherm of Secursol UHP Ca^{2+} -homoionic saturated montmorillonite (Sec_Ca)

At 95% r.h., both branches reach approximately 19.0 Å, consistent with extensive hydration and a strongly developed trihydrated (3W-like) configuration. Nevertheless, this spacing does not prove a homogeneous 3W structure. Chaaya et al. (2023) reported approximately 64% 3W and 28% 2W layers in Ca-exchanged smectite at 95% r.h., demonstrating that substantial hydration can coexist with multiple interlayer configurations. These proportions should not be transferred directly to Secursol UHP because the experimental conditions and material characteristics may differ.

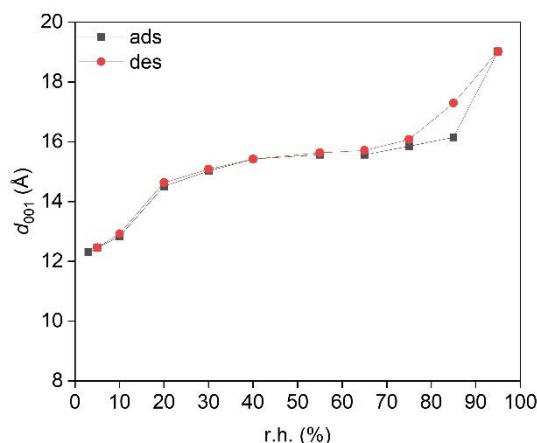


Figure 6.29: d_{001} Secursol UHP Ca^{2+} -homoionic saturated montmorillonite (Sec_Ca) as function of r.h.

The adsorption–desorption comparison reveals pronounced hydration hysteresis, particularly at 85% r.h., where d_{001} is approximately 16.1 Å during adsorption and 17.3 Å during desorption, giving a difference of about 1.2 Å. At 95% r.h., the branches converge at 19.0 Å, suggesting that structural differences between the two pathways become less evident under the highest-humidity conditions. This hysteresis may involve reorganisation of Ca^{2+} hydration shells, changes in water distribution, hydrogen bonding, and kinetic limitations during hydration and dehydration. Molecular simulations support these mechanisms as plausible explanations, although their individual contributions have not been directly measured in the present sample (Ferrage et al., 2007a, 2007b; Wang et al., 2025).

Sec_Ca progresses from predominantly 1W-like hydration at low r.h. through a 1W–2W transition and a 2W-dominated regime at intermediate r.h. towards a highly hydrated, 3W-like configuration at 95% r.h.. The pronounced hysteresis at 85% r.h. demonstrates that basal expansion depends on both water activity and the preceding hydration–dehydration history. These findings reflect the combined influence of Ca^{2+} –water interactions, interlayer organisation, and hydration-state heterogeneity.

XRD patterns of Secursol UHP Mg^{2+} - homoionic saturated montmorillonite (Sec_Mg) show a shift of the basal (001) reflection towards lower 2θ values as r.h. increases, indicating interlayer expansion due to water uptake (Figure 6.30). During adsorption, the basal spacing d_{001} increases from approximately 12.3 Å at 3% r.h. to 12.8–12.9 Å at 10% r.h., 14.5 Å at 20% r.h., and 15.0–15.6 Å at 30–65% r.h.. It subsequently reaches 15.9–16.1 Å at 75–85% r.h. and approximately 19.0 Å at 95% r.h.. During desorption, d_{001} increases from approximately 12.5–12.9 Å at 5–10% r.h. to 14.6 Å at 20% r.h., 15.1–15.7 Å at 30–65% r.h., and 16.0 and 17.3 Å at 75% and 85% r.h., respectively (Figure 6.31). Both branches converge at approximately 19.0 Å at 95% r.h., demonstrating progressive hydration and a path-dependent structural response (Ferrage et al., 2005; Yotsuji et al., 2021).

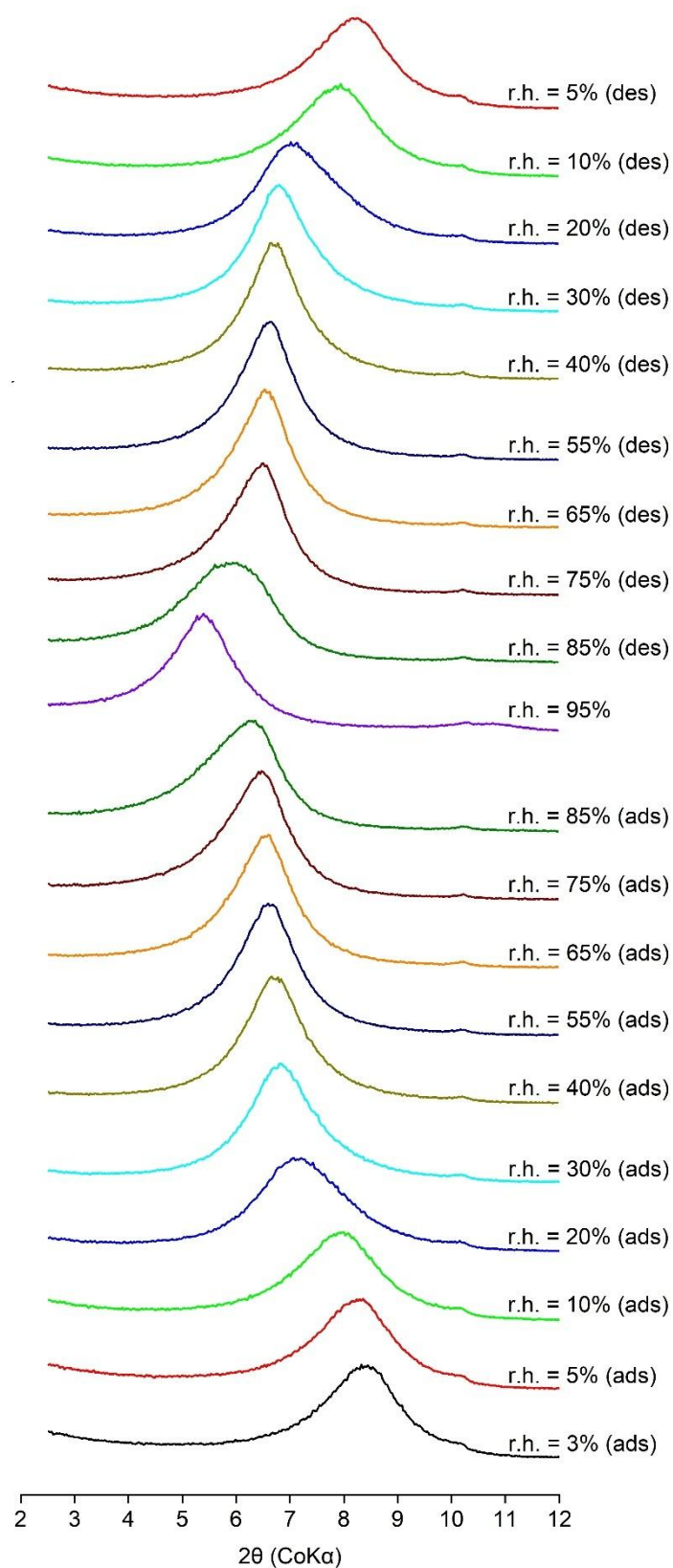


Figure 6.30: XRD isotherm of Secursol UHP Mg^{2+} -homoionic saturated montmorillonite (Sec_Mg)

At low r.h., basal spacings of approximately 12.3–12.9 Å are consistent with predominantly monohydrated (1W-like) configurations rather than a dehydrated zero-water-layer (0W) state. This indicates that interlayer water remains associated with the clay under relatively dry conditions. The strong hydration affinity of Mg^{2+} may contribute to this behaviour through interactions with water molecules and the negatively charged clay surfaces. However, the precise r.h. at which the initial 0W–1W transition occurs cannot be determined because the lowest measured spacings are already within the 1W-like range. These assignments describe the dominant hydration behaviour rather than establish a uniform structure throughout the crystallites (Ferrage et al., 2005).

Between 20% and 30% r.h., d_{001} increases to approximately 14.5–15.0 Å, indicating a transition towards bihydrated (2W-like) configurations. From 30% to 65% r.h., spacings of approximately 15.0–15.6 Å are consistent with a predominantly 2W-like regime. The gradual expansion may reflect changes in water distribution, Mg^{2+} hydration shells, and interlayer thickness, rather than the abrupt formation of additional complete water layers. Broad or asymmetric basal reflections may also indicate the coexistence of differently hydrated interlayers. XRD profile modelling has demonstrated that such heterogeneity is common during transitions between hydration states (Ferrage et al., 2005).

At 75–85% r.h., adsorption produces spacings of approximately 15.9–16.1 Å, whereas desorption reaches 16.0 Å at 75% r.h. and 17.3 Å at 85% r.h.. The latter value indicates a transition towards more highly hydrated configurations but does not establish a homogeneous trihydrated (3W) state. At 95% r.h., both branches reach approximately 19.0 Å, consistent with extensive hydration and a strongly developed 3W-like configuration. Nevertheless, 2W and 3W layers may coexist. Accordingly, quantitative determination of their relative proportions requires modelling the complete XRD profiles rather than relying solely on the maximum (001) reflection (Ferrage et al., 2005; Chaaya et al., 2023).

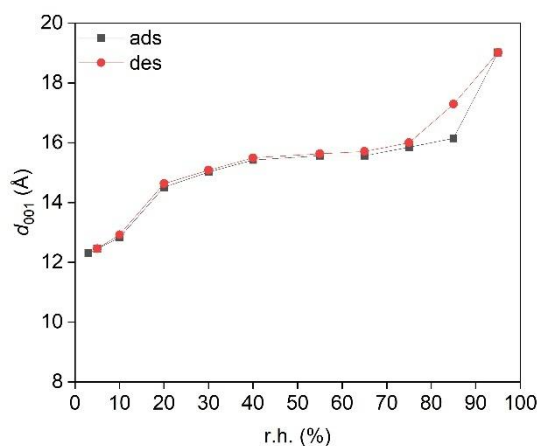


Figure 6.31: d_{001} Secursol UHP Mg^{2+} -homoionic saturated montmorillonite (Sec_Mg) as function of r.h.

Comparison of the adsorption and desorption branches reveals hydration hysteresis, most clearly at 85% r.h., where d_{001} reaches 16.1 Å during adsorption and 17.3 Å during desorption, giving a difference of approximately 1.2 Å. By comparison, the difference at 30% r.h. is only approximately 0.1 Å. The branches converge at 19.0 Å at 95% RH, indicating that their structural differences become less apparent at the highest humidity. This behaviour suggests that the interlayer structure depends on the preceding hydration–dehydration pathway. Possible mechanisms include the reorganisation of Mg^{2+} hydration shells, changes in water-molecule distribution, hydrogen bonding, and kinetic limitations

during water uptake and release. These mechanisms are plausible explanations, but their individual contributions cannot be established from the present XRD data alone (Yotsuji et al., 2021).

The hydration response must also be considered in the context of Secursol UHP's intrinsic mineralogy and microstructure. Characterisation of Secursol UHP and Calcigel indicates differences in smectite content, layer charge, particle-size distribution, basal surface area, and crystallite stacking. Secursol UHP also exhibits an inherited-fabric effect that can restrict smectite expansion despite its relatively high smectite content (Asaad et al., 2025). Consequently, its d_{001} response reflects not only Mg^{2+} hydration but also the effects of layer charge, water accessibility, and aggregate structure.

Sec_Mg progresses from predominantly 1W-like hydration at low r.h. through a 1W–2W transition and a 2W-dominated regime at intermediate r.h. towards a highly hydrated, 3W-like configuration at 95% RH. The pronounced hysteresis at 85% r.h. demonstrates that basal expansion depends on both water activity and hydration history. These findings indicate that interlayer hydration is governed by the combined effects of Mg^{2+} –water–surface interactions, hydration-state heterogeneity, and the intrinsic microstructure of the montmorillonite.

Overall Hydration Behaviour of the Montmorillonite Samples, the XRD results indicate that montmorillonite hydration is a stepwise yet heterogeneous process that depends on the hydration history of the sample. It is governed primarily by the identity and valence of the interlayer cations and is further influenced by layer charge, crystallite stacking, particle-size distribution, and the inherited fabric of the parent bentonite. In the present dataset, K^+ -saturated systems exhibit the most restricted basal expansion, generally progressing from 0W to 1W, whereas Na^+ -saturated systems display a pronounced progression from 0W through 1W and 2W towards a 3W-like configuration at high r.h.. By contrast, Ca^{2+} - and Mg^{2+} -saturated systems retain interlayer water at low r.h. and generally, evolve from 1W-like configurations towards 2W- and ultimately 3W-like states as humidity increases. Differences between the adsorption and desorption branches further demonstrate that d_{001} is not uniquely determined by r.h., because the interlayer structure also depends on hydration history, cation–water reorganisation, and kinetic constraints. Importantly, the measured d_{001} represents an apparent basal spacing and does not, by itself, establish a homogeneous hydration state. Quantitative determination of the proportions of 0W, 1W, 2W, and 3W layers requires modelling of the complete XRD profiles, particularly the 00l reflections. Thus, changes in d_{001} provide a key crystallographic indicator linking interlayer-cation identity, water organisation, basal expansion, and montmorillonite hydration and swelling mechanisms (Ferrage et al., 2005; Yotsuji et al., 2021).

Comparison of Calcigel and Secursol UHP demonstrates that the interlayer cation is not the sole determinant of hydration behaviour. Even when the same cation is present, the two bentonites exhibit differences in their d_{001} – r.h. responses, indicating an additional influence from the intrinsic characteristics of the parent mineral. Secursol UHP contains approximately 79% dioctahedral smectite, compared with approximately 61% in Calcigel. The smectites in both materials have been characterised as montmorillonitic–beidellitic, with significant octahedral iron. Secursol UHP has a slightly higher layer charge and a broader particle-size distribution, whereas Calcigel exhibits an approximately 25% larger average basal surface and slightly greater layer-stack thickness. Despite its lower smectite content, Calcigel displays greater water uptake and better dispersibility in deionised water. These differences have been attributed to the inherited fabric of Secursol UHP, which restricts smectite expansion. Consequently, the hydration behaviour of natural and homoionically saturated bentonites reflects the combined effects of cation chemistry, layer charge, particle-size distribution, crystallite stacking, and aggregate microstructure rather than cation identity alone (Asaad et al., 2025).

Table 6.2: Comparative hydration patterns of raw and homoionic saturated montmorillonite Calcigel and Secursol UHP under varying r.h.

Sample	Interlayer cation	Low r.h.	Intermediate r.h.	High r.h.	Overall hydration pattern	Key characteristics
Cal_R	Naturally occurring $\text{Ca}^{2+}/\text{Mg}^{2+}$	1W	1W/2W $\rightarrow$ 2W	2W/3W $\rightarrow$ 3W	1W $\rightarrow$ 1W/2W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	Relatively hydrated at low r.h.; 2W dominates at intermediate r.h.
Cal_Na	Na^+	0W	0W/1W $\rightarrow$ 1W	1W $\rightarrow$ 2W $\rightarrow$ 3W	0W $\rightarrow$ 1W $\rightarrow$ 2W $\rightarrow$ 3W	Pronounced basal expansion and progressive hydration transitions.
Cal_K	K^+	0W	0W/1W $\rightarrow$ 1W	1W	0W $\rightarrow$ 1W	Most restricted swelling; 2W and 3W are not dominant.
Cal_Ca	Ca^{2+}	1W	1W/2W $\rightarrow$ 2W	2W/3W $\rightarrow$ 3W	1W $\rightarrow$ 1W/2W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	Similar to the naturally Ca/Mg-rich material; 2W dominates at intermediate r.h.
Cal_Mg	Mg^{2+}	1W-like	1W/2W $\rightarrow$ 2W	2W/3W $\rightarrow$ 3W*	1W-like $\rightarrow$ 1W/2W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W*	Retains interlayer hydration at low r.h.; expands substantially more than the K^+ form.
Sec_R	Naturally occurring $\text{Ca}^{2+}/\text{Mg}^{2+}$	1W	1W/2W $\rightarrow$ 2W	2W/3W $\rightarrow$ 3W	1W $\rightarrow$ 1W/2W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	Hydration is influenced by inherited fabric and the heterogeneity of the natural mineral assemblage.
Sec_Na	Na^+	0W	0W/1W $\rightarrow$ 1W	1W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	0W $\rightarrow$ 1W $\rightarrow$ 2W $\rightarrow$ 3W	Progressive hydration with pronounced hysteresis, particularly at intermediate r.h.
Sec_K	K^+	0W	0W/1W $\rightarrow$ 1W	1W	0W $\rightarrow$ 1W	Strongly restricted expansion; the 1W-like state persists at high r.h.
Sec_Ca	Ca^{2+}	1W	1W/2W $\rightarrow$ 2W	2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	1W $\rightarrow$ 1W/2W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	Early hydration and pronounced expansion towards a 3W-like state at 95% r.h.
Sec_Mg	Mg^{2+}	1W	1W/2W $\rightarrow$ 2W	2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	1W $\rightarrow$ 1W/2W $\rightarrow$ 2W $\rightarrow$ 2W/3W $\rightarrow$ 3W	Strong hydration affinity; progressive expansion towards a 3W-like configuration at high RH.

Comparative hydration patterns of raw and homoionic saturated montmorillonite of Calcigel and Secursol UHP under varying relative humidity summarized in Table 6.2. The differences between the adsorption and desorption branches demonstrate that d_{001} depends on both r.h. and hydration history. Hysteresis is particularly evident in the Na^+ -saturated systems at intermediate r.h. and in some divalent-cation systems at higher r.h.. This non-coincidence indicates that changes in interlayer structure are not fully reversible along an identical pathway. Reorganisation of interlayer cations, redistribution of water molecules, changes in hydrogen-bond networks, and kinetic limitations during water uptake and release may all contribute to this behaviour. In situ X-ray scattering and molecular simulation studies support the relationship between interlayer hydration, swelling, and the organisation of water and exchangeable cations. Research on Ca-montmorillonite has also highlighted the role of cation hydration and hydrogen bonding in adsorption–desorption hysteresis (Chaaya et al., 2023; Wang et al., 2025). Nevertheless, the relative contribution of these mechanisms cannot be established from basal-spacing measurements alone.

The ten samples exhibit a consistent qualitative hierarchy in which K^+ produces the most restricted crystalline swelling, Na^+ shows a pronounced stepwise transition from dehydrated to highly hydrated configurations, and Ca^{2+} and Mg^{2+} retain interlayer water at comparatively low r.h. before progressing towards 2W- and 3W-like states at higher humidity. However, these trends should not be interpreted as a universal ranking of swelling behaviour independent of the host mineral. Differences between Calcigel and Secursol UHP demonstrate that layer charge, particle-size distribution, crystallite stacking, and inherited fabric can modify the response associated with a given interlayer cation. Furthermore, the adsorption–desorption hysteresis confirms that hydration is path-dependent, while broad basal reflections and intermediate d_{001} values may indicate heterogeneous populations of interlayers. Accordingly, montmorillonite hydration is best understood as a stepwise but heterogeneous structural process governed principally by interlayer-cation identity and valence, and modified by the intrinsic properties of the host bentonite. Basal spacing is therefore a key crystallographic indicator of changes in the coupled cation–water–montmorillonite system, rather than a simple measure of increasing water content.

6.4 Summary, Conclusion and Future Outlook

6.4.1 Summary

The results show that Calcigel contains a finer fraction ($<2\ \mu\text{m}$, 58-65%) and higher dispersibility than Secursol UHP (56-57%), indicating more expandable layers. During dialysis, both clays exhibited high initial conductivity that decreased and stabilized after ~ 150 hours, confirming successful removal of soluble salts and completion of homoionic saturation. Na^+ and K^+ -homoionic saturated montmorillonite displayed higher conductivity and mobility than Ca^{2+} and Mg^{2+} types, reflecting weaker electrostatic binding.

CEC and hydration tests revealed that Secursol UHP has a higher exchange capacity and moisture content than Calcigel. Na^+ and K^+ forms showed high exchange efficiency but limited swelling in K^+ due to its low hydration energy, whereas Ca^{2+} and Mg^{2+} exhibited strong electrostatic attraction, higher water content, and structural stability. Water adsorption increased progressively with relative humidity, with Secursol UHP samples always retaining more water. Na^+ and Mg^{2+} exchanged montmorillonites absorbed the most moisture due to their high hydration energies.

Water-vapour sorption in Calcigel and Secursol UHP bentonites depends on exchangeable cations and parent-material characteristics. All samples exhibit nonlinear water uptake and adsorption–desorption hysteresis. At 97% relative humidity, Secursol UHP generally retains more water, whereas K^+ -homoionic saturated montmorillonite samples show the lowest water contents.

X-ray diffraction (XRD) analysis confirmed that montmorillonite undergoes stepwise swelling as relative humidity increases, characterised by successive transitions between zero-water-layer (0W), monohydrated (1W), bihydrated (2W), and trihydrated (3W)-like configurations. The overall hydration patterns depend on the exchangeable cation and the intrinsic properties of the parent bentonite. K^+ -saturated samples exhibit the most restricted expansion, generally remaining in a 1W-like state, whereas Na^+ -saturated samples show pronounced swelling towards 3W-like configurations at high humidity. Ca^{2+} - and Mg^{2+} -saturated samples retain interlayer water at low humidity and generally progress from 1W-like to 2W- and 3W-like configurations, although the final hydration state of Cal_Mg remains uncertain. Differences between adsorption and desorption further demonstrate hydration hysteresis, indicating that interlayer expansion depends on hydration history.

6.4.2 Conclusion

Calcigel and Secursol UHP montmorillonites exhibit distinct hydration and exchange behaviours influenced by cation type and clay structure. Secursol UHP, with higher CEC and finer smectitic composition, shows greater water retention and exchange efficiency. Na^+ and Mg^{2+} cations promote the highest swelling and hydration, while K^+ restricts interlayer expansion. The observed hysteresis in XRD patterns confirms partially reversible hydration–dehydration governed by cation–water interactions and mesoporous retention. Water-vapour sorption in Calcigel and Secursol UHP bentonites reflects the combined effects of exchangeable cations and parent-material characteristics, with nonlinear water uptake, adsorption–desorption hysteresis, and lower final water contents in K^+ -saturated samples. Montmorillonite swelling and purification efficiency are controlled by cation

valence, hydration energy, and layer charge, with Secursol UHP demonstrating superior ion-exchange and hydration performance. X-ray diffraction (XRD) analysis confirmed that montmorillonite undergoes stepwise swelling with increasing relative humidity, characterised by successive transitions between zero-water-layer (0W), monohydrated (1W), bihydrated (2W), and trihydrated (3W)-like configurations rather than continuous interlayer expansion.

6.4.3 Future Outlook

The comparative analysis of Calcigel and Secursol UHP montmorillonites highlights the complex interplay between mineralogy, cation type, and hydration dynamics. To build upon these findings, several research directions can be pursued to deepen understanding and enhance practical applications:

1. **Comprehensive Structural–Functional Correlation.** Future work should integrate microscopic (TEM, AFM) and spectroscopic (FTIR, NMR) analyses to better link structural features—such as layer stacking, pore morphology, and cation coordination—with macroscopic properties like swelling pressure, exchange kinetics, and moisture retention.
2. **Dynamic Hydration and Desorption Studies.** Conducting in situ XRD or thermogravimetric analyses (TGA) under controlled humidity and temperature would clarify the mechanisms of hysteresis and water retention, distinguishing between interlayer and mesopore contributions during hydration–dehydration cycles.
3. **Mixed-Cation and Natural System Modeling.** Because natural clays rarely exist in homoionic form, future research should explore mixed-cation montmorillonites (e.g., $\text{Na}^+/\text{Ca}^{2+}$ or $\text{Mg}^{2+}/\text{K}^+$ systems) to assess competitive ion exchange, cooperative hydration effects, and long-term stability under variable environmental conditions.
4. **Application-Oriented Testing.** The superior hydration and exchange capacity of Secursol UHP suggest potential for environmental and industrial applications such as contaminant adsorption, bentonite barrier systems, and water purification. Tailoring cation composition could optimize performance for specific uses, including heavy metal removal, ion buffering, and controlled moisture regulation.
5. **Thermodynamic and Kinetic Modelling.** Future studies should incorporate isothermal adsorption modelling and kinetic exchange simulations to quantify energy barriers and predict swelling–deswelling behaviour under cyclic or multicomponent conditions, linking experimental data to predictive performance models.
6. **Nanoengineering and Composite Development.** The distinct hydration responses of Calcigel and Secursol UHP offer opportunities for designing clay-based nanocomposites with swelling and adsorption properties. Functionalizing these clays with polymers or metal oxides could enhance their mechanical stability and selectivity for catalytic, environmental, or membrane technologies.

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List of Abbreviations

DFT	Density Functional Theory
QM	Quantum Mechanics
MD	Molecular Dynamics
UC	Unit Cell
tv	trans-vacant
cv	cis-vacant
FU	Formula Unit
CEC	Cation Exchange Capacity
GGA	Generalized Gradient Approximation
PBE	Perdew-Burke-Ernzerhof
PAW	Projector Augmented Wave
VESTA	Visualization for Electronic and Structural Analysis
TE	Total Energy
E-Map	Energy Mapping

Supplementary Materials

Table S1: Total energy of *tv Mg_{cis}* Na⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
4x1x1	4	8	0.125	20.72	8.98	9.65	1795.53	-1202.1408
2x2x1	4	8	0.125	10.36	17.96	9.65	1795.53	-1202.0207
1x4x1	4	8	0.125	5.18	35.92	9.65	1795.53	-1196.4832
2x1x1	2	4	0.25	10.36	8.98	9.65	897.77	-601.3964
1x2x1	2	4	0.25	5.18	17.96	9.65	897.77	-598.5882
4x1x1	4	8	0.375	20.72	8.98	9.65	1795.53	-1203.6980
2x2x1	4	8	0.375	10.36	17.96	9.65	1795.53	-1203.6576
1x4x1	4	8	0.375	5.18	35.92	9.65	1795.53	-1198.1760
2x1x1	2	4	0.5	10.36	8.98	9.65	897.77	-602.2196
1x2x1	2	4	0.5	5.18	17.96	9.65	897.77	-599.6188
1x1x1	1	2	0.5	5.18	8.98	9.65	448.88	-299.6995

Table S2: Total energy of *cv Mg_{cis}* Na⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
4x1x1	4	8	0.125	20.72	8.98	9.65	1795.53	-1202.2403
2x2x1	4	8	0.125	10.36	17.96	9.65	1795.53	-1202.2126
1x4x1	4	8	0.125	5.18	35.92	9.65	1795.53	-1196.9809
2x1x1	2	4	0.25	10.36	8.98	9.65	897.77	-601.5103
1x2x1	2	4	0.25	5.18	17.96	9.65	897.77	-598.8759
4x1x1	4	8	0.375	20.72	8.98	9.65	1795.53	-1204.1350
2x2x1	4	8	0.375	10.36	17.96	9.65	1795.53	-1204.1186
1x4x1	4	8	0.375	5.18	35.92	9.65	1795.53	-1198.7259
2x1x1	2	4	0.5	10.36	8.98	9.65	897.77	-602.4665
1x2x1	2	4	0.5	5.18	17.96	9.65	897.77	-599.8030
1x1x1	1	2	0.5	5.18	8.98	9.65	448.88	-299.7901

Table S3: Total energy of *cv Mg_{trans}* Na⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
4x1x1	4	8	0.125	20.72	8.98	9.65	1795.53	-1202.1997
2x2x1	4	8	0.125	10.36	17.96	9.65	1795.53	-1202.2070
1x4x1	4	8	0.125	5.18	35.92	9.65	1795.53	-1197.0176
2x1x1	2	4	0.25	10.36	8.98	9.65	897.77	-601.4948
1x2x1	2	4	0.25	5.18	17.96	9.65	897.77	-598.9011
4x1x1	4	8	0.375	20.72	8.98	9.65	1795.53	-1204.0124
2x2x1	4	8	0.375	10.36	17.96	9.65	1795.53	-1204.0683
1x4x1	4	8	0.375	5.18	35.92	9.65	1795.53	-1198.7676
2x1x1	2	4	0.5	10.36	8.98	9.65	897.77	-602.4180
1x2x1	2	4	0.5	5.18	17.96	9.65	897.77	-599.8047
1x1x1	1	2	0.5	5.18	8.98	9.65	448.88	-299.7909

Table S4: Total energy of *tv Mg_{cis}* K⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
4x1x1	4	8	0.125	20.72	8.98	10.25	1907.17	-1201.8511
2x2x1	4	8	0.125	10.36	17.96	10.25	1907.17	-1201.8431
1x4x1	4	8	0.125	5.18	35.92	10.25	1907.17	-1196.0880
2x1x1	2	4	0.25	10.36	8.98	10.25	953.59	-601.2467
1x2x1	2	4	0.25	5.18	17.96	10.25	953.59	-598.3762
4x1x1	4	8	0.375	20.72	8.98	10.25	1907.17	-1203.5723
2x2x1	4	8	0.375	10.36	17.96	10.25	1907.17	-1203.6013
1x4x1	4	8	0.375	5.18	35.92	10.25	1907.17	-1197.5804
2x1x1	2	4	0.5	10.36	8.98	10.25	953.59	-602.1040
1x2x1	2	4	0.5	5.18	17.96	10.25	953.59	-599.3024
1x1x1	1	2	0.5	5.18	8.98	10.25	476.79	-299.5349

Table S5: Total energy *cv Mg_{cis}* K⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
4x1x1	4	8	0.125	20.72	8.98	10.10	1879.26	-1201.9728
2x2x1	4	8	0.125	10.36	17.96	10.10	1879.26	-1201.9939
1x4x1	4	8	0.125	5.18	35.92	10.10	1879.26	-1196.8585
2x1x1	2	4	0.25	10.36	8.98	10.10	939.63	-601.3340
1x2x1	2	4	0.25	5.18	17.96	10.10	939.63	-598.8151
4x1x1	4	8	0.375	20.72	8.98	10.10	1879.26	-1203.9520
2x2x1	4	8	0.375	10.36	17.96	10.10	1879.26	-1203.9948
1x4x1	4	8	0.375	5.18	35.92	10.10	1879.26	-1198.4505
2x1x1	2	4	0.5	10.36	8.98	10.10	939.63	-602.3380
1x2x1	2	4	0.5	5.18	17.96	10.10	939.63	-599.6477
1x1x1	1	2	0.5	5.18	8.98	10.10	469.82	-299.7089

Table S6: Total energy of *cv Mg_{trans}* K⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
4x1x1	4	8	0.125	20.72	8.98	10.10	1879.26	-1201.9515
2x2x1	4	8	0.125	10.36	17.96	10.10	1879.26	-1201.9974
1x4x1	4	8	0.125	5.18	35.92	10.10	1879.26	-1196.8714
2x1x1	2	4	0.25	10.36	8.98	10.10	939.63	-601.3303
1x2x1	2	4	0.25	5.18	17.96	10.10	939.63	-598.8152
4x1x1	4	8	0.375	20.72	8.98	10.10	1879.26	-1203.8850
2x2x1	4	8	0.375	10.36	17.96	10.10	1879.26	-1203.9349
1x4x1	4	8	0.375	5.18	35.92	10.10	1879.26	-1198.4164
2x1x1	2	4	0.5	10.36	8.98	10.10	939.63	-602.2831
1x2x1	2	4	0.5	5.18	17.96	10.10	939.63	-599.6013
1x1x1	1	2	0.5	5.18	8.98	10.10	469.82	-299.6858

Table S7: Total energy of *tv Mg_{cis}* Ca²⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
8x1x1	8	16	0.125	41.44	8.98	9.65	3591.07	-2402.9782
4x2x1	8	16	0.125	20.72	17.96	9.65	3591.07	-2403.2475
2x4x1	8	16	0.125	10.36	35.92	9.65	3591.07	-2402.9268
4x1x1	4	8	0.250	20.72	8.98	9.65	1795.53	-1201.5843
2x2x1	4	8	0.250	10.36	17.96	9.65	1795.53	-1201.4995
8x1x1	8	16	0.375	41.44	8.98	9.65	3591.07	-2403.1781
4x2x1	8	16	0.375	20.72	17.96	9.65	3591.07	-2403.7795
2x4x1	8	16	0.375	10.36	35.92	9.65	3591.07	-2403.1932
4x1x1	4	8	0.500	20.72	8.98	9.65	1795.53	-1201.8430
2x2x1	4	8	0.500	10.36	17.96	9.65	1795.53	-1201.8445

Table S8: Total energy of *cv Mg_{cis}* Ca²⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
8x1x1	8	16	0.125	41.44	8.98	9.65	3591.07	-2402.9575
4x2x1	8	16	0.125	20.72	17.96	9.65	3591.07	-2403.3355
2x4x1	8	16	0.125	10.36	35.92	9.65	3591.07	-2403.0165
4x1x1	4	8	0.250	20.72	8.98	9.65	1795.53	-1201.6514
2x2x1	4	8	0.250	10.36	17.96	9.65	1795.53	-1201.6446
8x1x1	8	16	0.375	41.44	8.98	9.65	3591.07	-2403.6853
4x2x1	8	16	0.375	20.72	17.96	9.65	3591.07	-2404.1467
2x4x1	8	16	0.375	10.36	35.92	9.65	3591.07	-2403.7692
4x1x1	4	8	0.500	20.72	8.98	9.65	1795.53	-1202.0463
2x2x1	4	8	0.500	10.36	17.96	9.65	1795.53	-1202.0648

Table S9: Total energy of *cv Mg_{trans}* Ca²⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å)	Total Energy (eV)
8x1x1	8	16	0.125	41.44	8.98	9.65	3591.07	-2402.9669
4x2x1	8	16	0.125	20.72	17.96	9.65	3591.07	-2403.1971
2x4x1	8	16	0.125	10.36	35.92	9.65	3591.07	-2402.7935
4x1x1	4	8	0.250	20.72	8.98	9.65	1795.53	-1201.6531
2x2x1	4	8	0.250	10.36	17.96	9.65	1795.53	-1201.4901
8x1x1	8	16	0.375	41.44	8.98	9.65	3591.07	-2403.2616
4x2x1	8	16	0.375	20.72	17.96	9.65	3591.07	-2403.9784
2x4x1	8	16	0.375	10.36	35.92	9.65	3591.07	-2403.2932
4x1x1	4	8	0.500	20.72	8.98	9.65	1795.53	-1202.0271
2x2x1	4	8	0.500	10.36	17.96	9.65	1795.53	-1202.0502

Table S10: Total energy of *tv Mg_{cis}* Mg²⁺-saturated montmorillonite

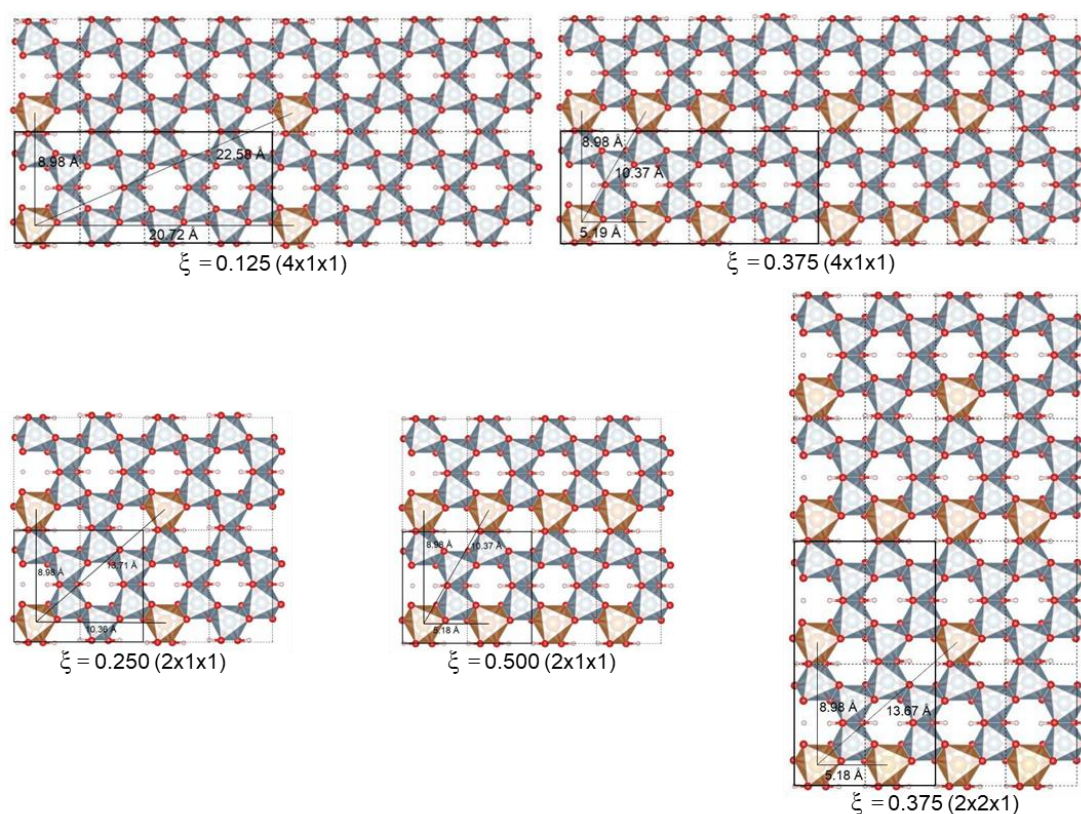
Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å)	Total Energy (eV)
8x1x1	8	16	0.125	41.44	8.98	9.65	3591.07	-2400.2253
4x2x1	8	16	0.125	20.72	17.96	9.65	3591.07	-2400.5629
2x4x1	8	16	0.125	10.36	35.92	9.65	3591.07	-2400.2411
4x1x1	4	8	0.250	20.72	8.98	9.65	1795.53	-1198.8362
2x2x1	4	8	0.250	10.36	17.96	9.65	1795.53	-1198.8182
8x1x1	8	16	0.375	41.44	8.98	9.65	3591.07	-2394.2365
4x2x1	8	16	0.375	20.72	17.96	9.65	3591.07	-2395.5281
2x4x1	8	16	0.375	10.36	35.92	9.65	3591.07	-2394.2932
4x1x1	4	8	0.500	20.72	8.98	9.65	1795.53	-1196.2926
2x2x1	4	8	0.500	10.36	17.96	9.65	1795.53	-1196.2960

Table S11: Total energy of *cv Mg_{cis}* Mg²⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å)	Total Energy (eV)
8x1x1	8	16	0.125	41.44	8.98	9.65	3591.07	-2400.1194
4x2x1	8	16	0.125	20.72	17.96	9.65	3591.07	-2400.5249
2x4x1	8	16	0.125	10.36	35.92	9.65	3591.07	-2400.2027
4x1x1	4	8	0.250	20.72	8.98	9.65	1795.53	-1198.8123
2x2x1	4	8	0.250	10.36	17.96	9.65	1795.53	-1198.8287
8x1x1	8	16	0.375	41.44	8.98	9.65	3591.07	-2394.5712
4x2x1	8	16	0.375	20.72	17.96	9.65	3591.07	-2395.6019
2x4x1	8	16	0.375	10.36	35.92	9.65	3591.07	-2394.7952
4x1x1	4	8	0.500	20.72	8.98	9.65	1795.53	-1196.3171
2x2x1	4	8	0.500	10.36	17.96	9.65	1795.53	-1196.3446

Table S12: Total energy of *cv Mg_{trans}* Mg²⁺-saturated montmorillonite

Supercell Model	UC	FU	ξ /FU	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Total Energy (eV)
8x1x1	8	16	0.125	41.44	8.98	9.65	3591.07	-2400.0941
4x2x1	8	16	0.125	20.72	17.96	9.65	3591.07	-2400.3542
2x4x1	8	16	0.125	10.36	35.92	9.65	3591.07	-2399.9620
4x1x1	4	8	0.250	20.72	8.98	9.65	1795.53	-1198.7842
2x2x1	4	8	0.250	10.36	17.96	9.65	1795.53	-1198.6606
8x1x1	8	16	0.375	41.44	8.98	9.65	3591.07	-2394.8932
4x2x1	8	16	0.375	20.72	17.96	9.65	3591.07	-2395.3725
2x4x1	8	16	0.375	10.36	35.92	9.65	3591.07	-2394.9422
4x1x1	4	8	0.500	20.72	8.98	9.65	1795.53	-1196.2705
2x2x1	4	8	0.500	10.36	17.96	9.65	1795.53	-1196.2938

Figure S1. Octahedral structure *tv Mg_{cis}* (substitution in orange) of Na⁺ and K⁺-saturated montmorillonite (dashed rim: unit cell, black rim: supercell)

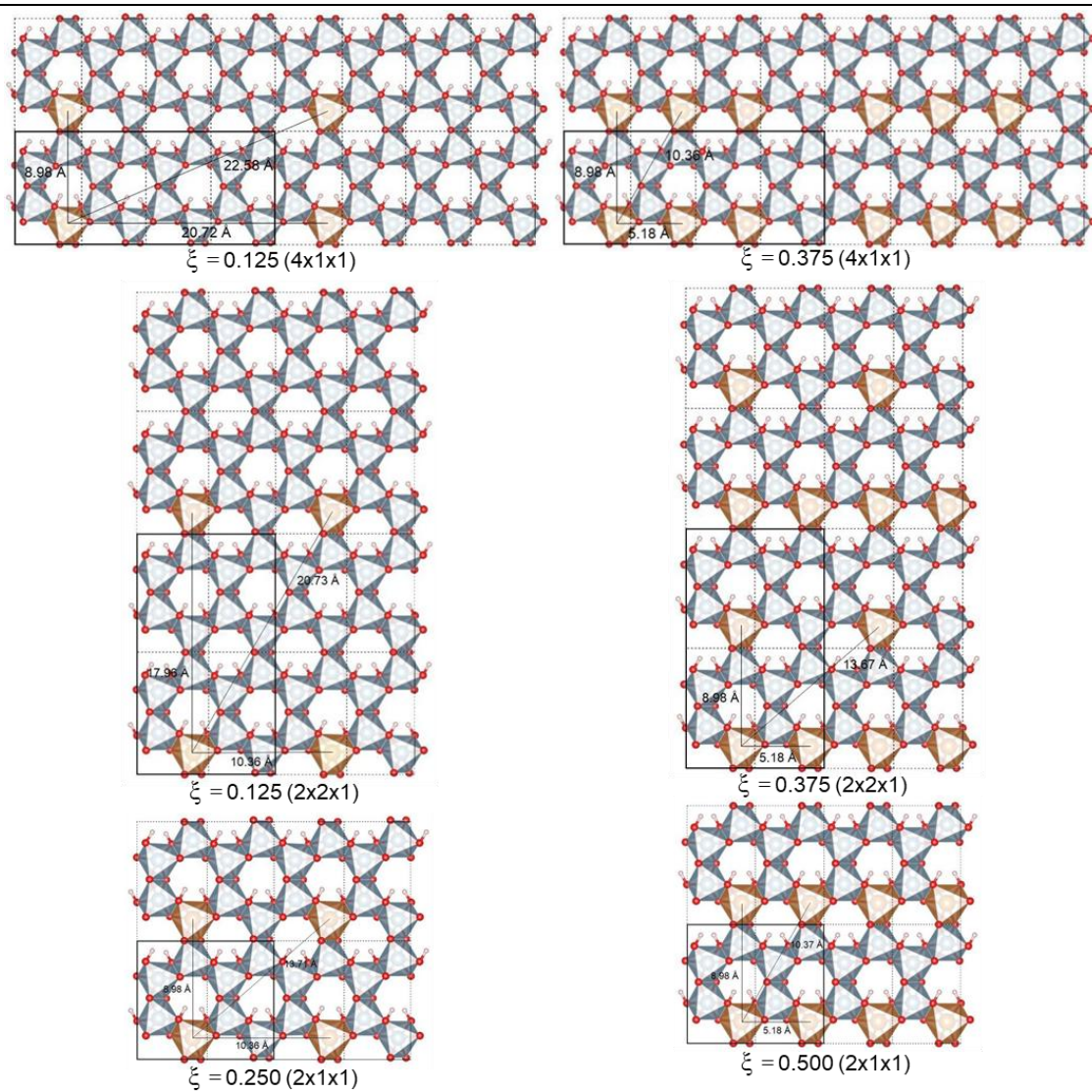


Figure S2. Octahedral structure cv Mg_{cis} (substitution in orange) of Na^+ and K^+ -saturated montmorillonite (dashed rim: unit cell, black rim: supercell)

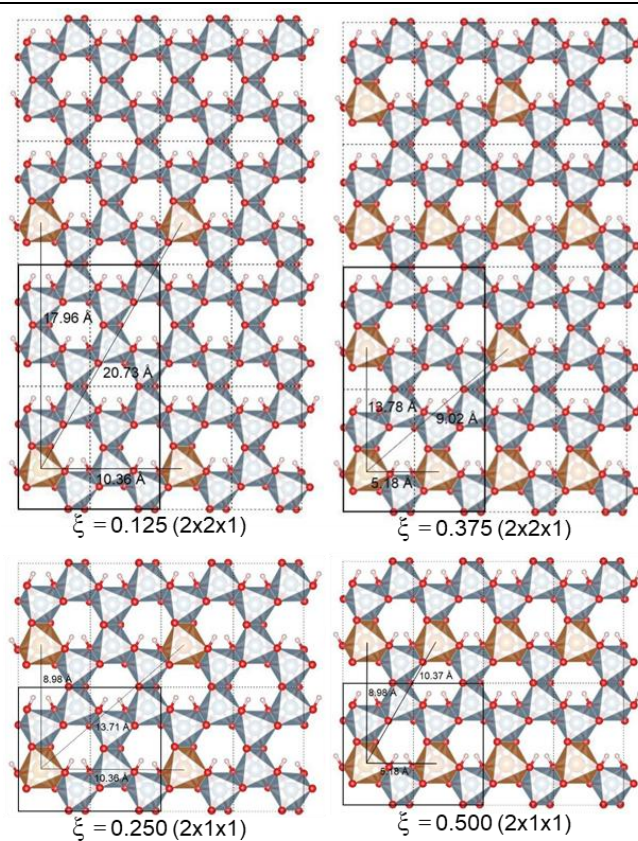


Figure S3. Octahedral structure cv Mg_{trans} (substitution in orange) of Na⁺ and K⁺-saturated montmorillonite (dashed rim: unit cell, black rim: supercell)

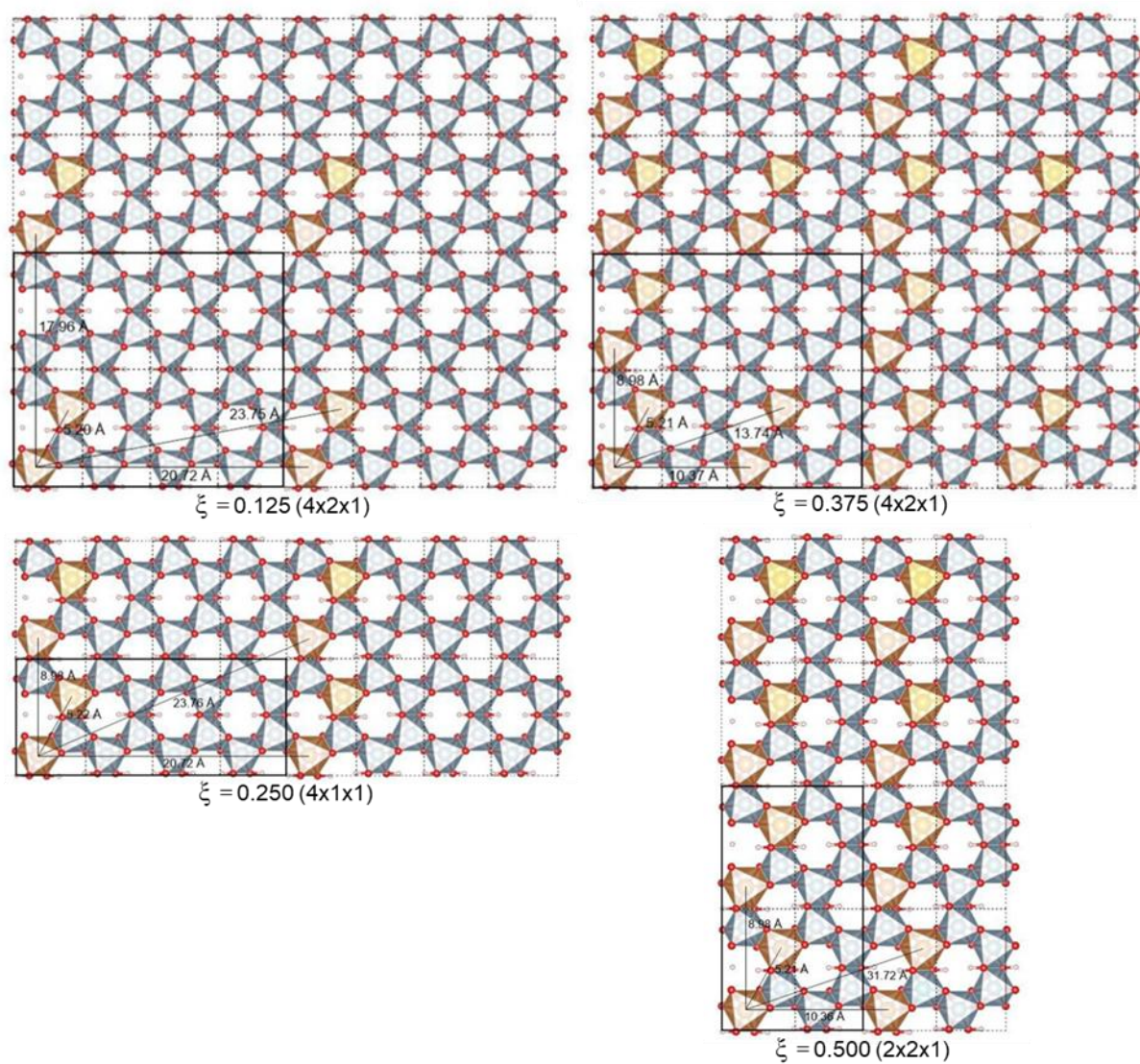


Figure S4. Octahedral structure *cv* Mg_{cis} (substitution in orange) of Ca^{2+} and Mg^{2+} -saturated montmorillonite (dashed rim: unit cell, black rim: supercell)

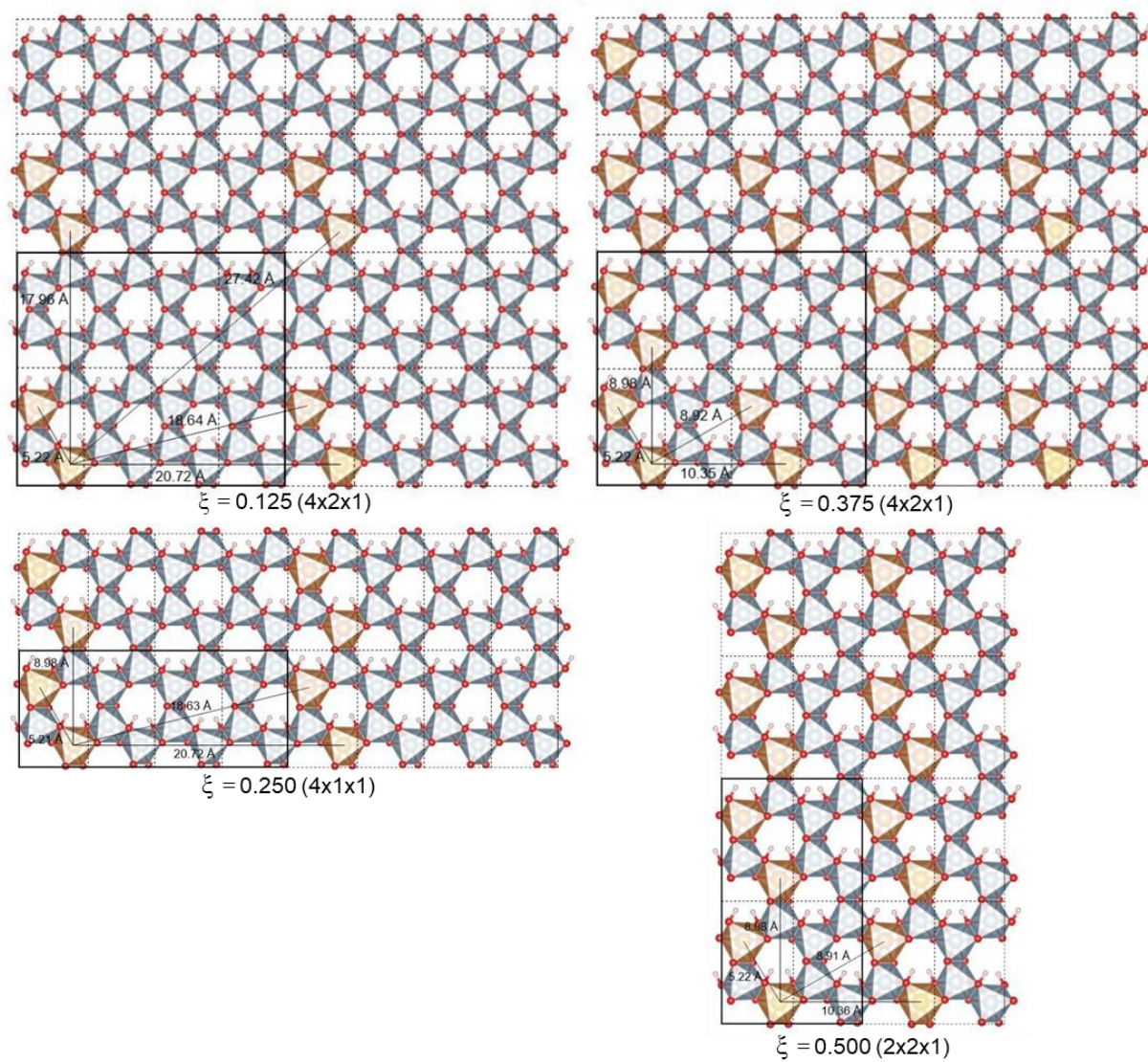


Figure S5. Octahedral structure tvMg_{cis} (substitution in orange) of Ca^{2+} and Mg^{2+} -saturated montmorillonite (dashed rim: unit cell, black rim: supercell)

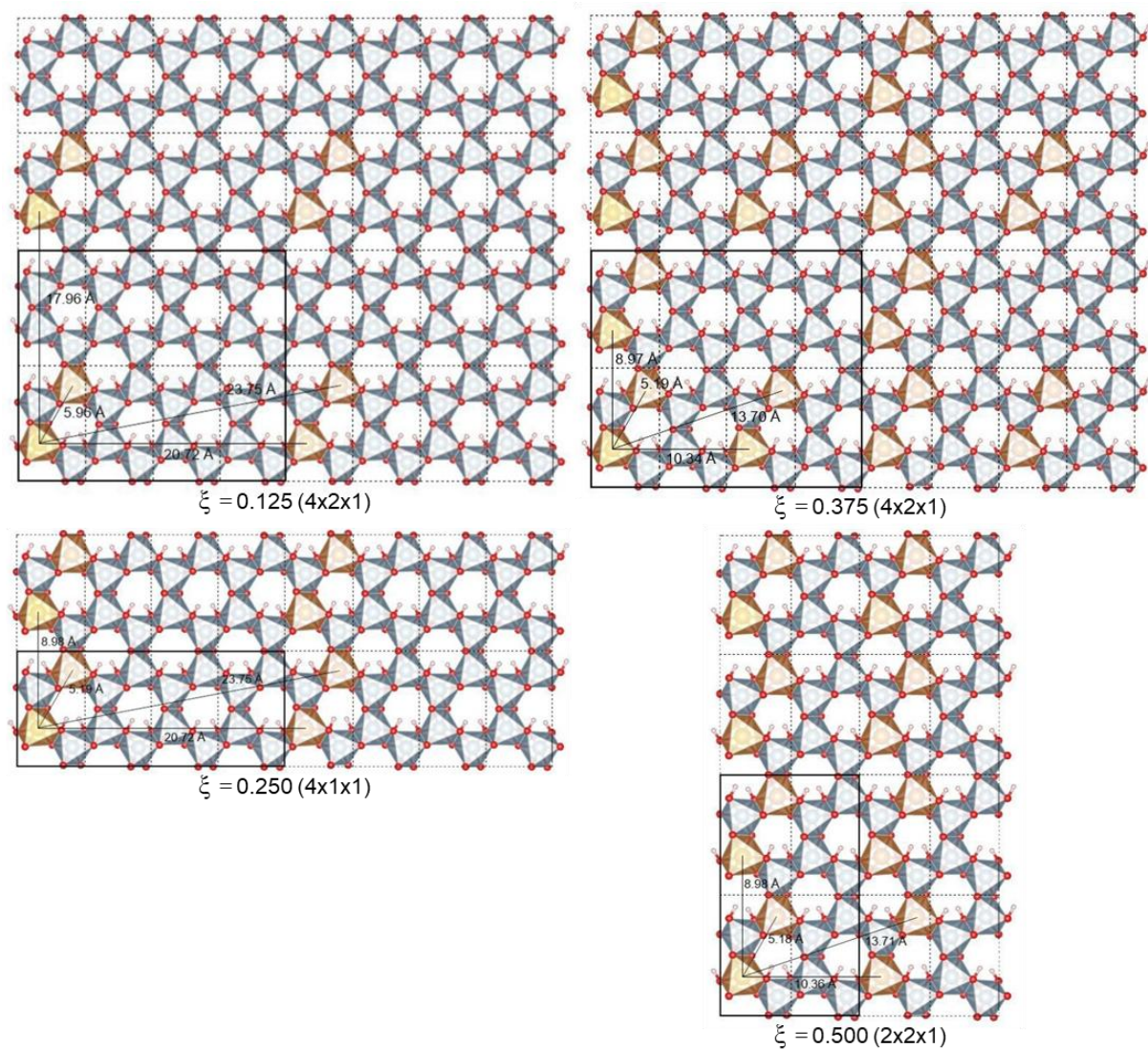


Figure S6. Structure cv Mg_{trans} (substitution in orange) of Ca^{2+} and Mg^{2+} -saturated montmorillonite (dashed rim: unit cell, black rim: supercell)

Table S13: d_{001} [Å] of Saturated Montmorillonite

	Layer Charge (ξ) = 0.125		Layer Charge (ξ) = 0.250		Layer Charge (ξ) = 0.375		Layer Charge (ξ) = 0.500	
Na ⁺ -saturated Montmorillonite								
	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell
<i>tv</i> Mg _{<i>cis</i>}	9.71	4x1x1	9.73	2x1x1	9.73	4x1x1	9.74	2x1x1
<i>cv</i> Mg _{<i>cis</i>}	9.65	4x1x1	9.68	2x1x1	9.66	4x1x1	9.67	2x1x1
<i>cv</i> Mg _{<i>trans</i>}	9.67	2x2x1	9.67	2x1x1	9.66	2x2x1	9.68	2x1x1
K ⁺ -saturated Montmorillonite								
	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell
<i>tv</i> Mg _{<i>cis</i>}	9.93	4x1x1	10.09	2x1x1	10.22	2x2x1	10.28	2x1x1
<i>cv</i> Mg _{<i>cis</i>}	9.88	2x2x1	10.02	2x1x1	10.13	2x2x1	10.16	2x1x1
<i>cv</i> Mg _{<i>trans</i>}	9.88	2x2x1	10.02	2x1x1	10.13	2x2x1	10.14	2x1x1
Ca ²⁺ -saturated Montmorillonite								
	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell
<i>tv</i> Mg _{<i>cis</i>}	9.70	4x2x1	9.66	4x1x1	9.68	4x2x1	9.57	2x2x1
<i>cv</i> Mg _{<i>cis</i>}	9.64	4x2x1	9.59	4x1x1	9.56	4x2x1	9.48	2x2x1
<i>cv</i> Mg _{<i>trans</i>}	9.64	4x2x1	9.59	4x1x1	9.57	4x2x1	9.47	2x2x1
Mg ²⁺ -saturated Montmorillonite								
	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell	d_{001} [Å]	Model Supercell
<i>tv</i> Mg _{<i>cis</i>}	9.71	4x2x1	9.67	4x1x1	9.67	4x2x1	9.57	2x2x1
<i>cv</i> Mg _{<i>cis</i>}	9.64	4x2x1	9.56	4x1x1	9.56	4x2x1	9.49	2x2x1
<i>cv</i> Mg _{<i>trans</i>}	9.62	4x2x1	9.58	4x1x1	9.60	4x2x1	9.55	2x2x1

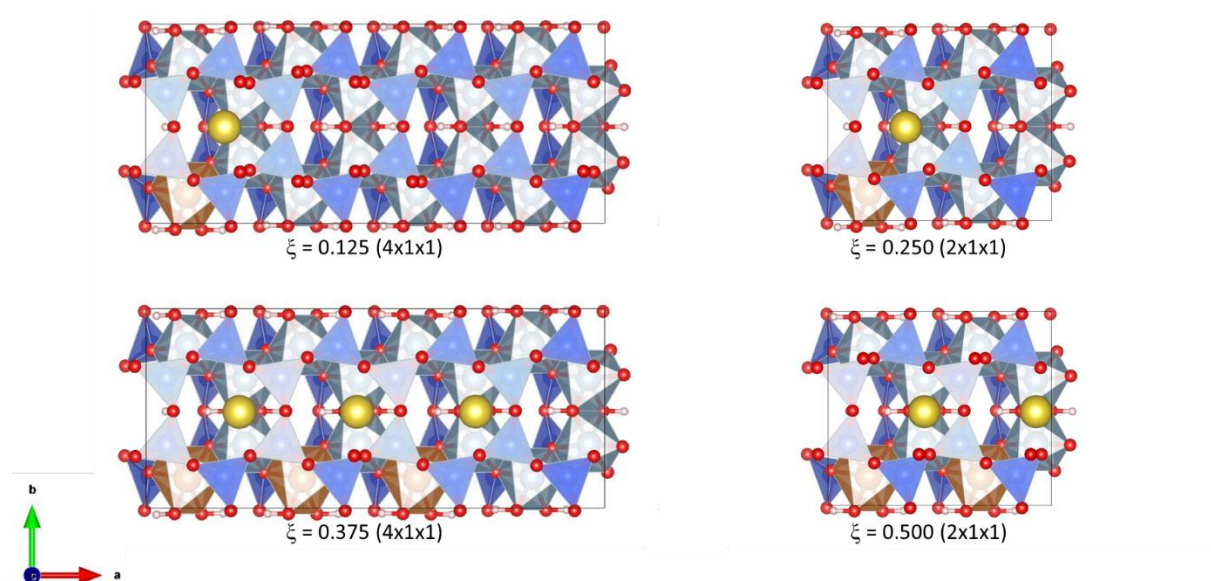


Figure S7. The most stable structure of *tv* Mg_{cis} Na^+ -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

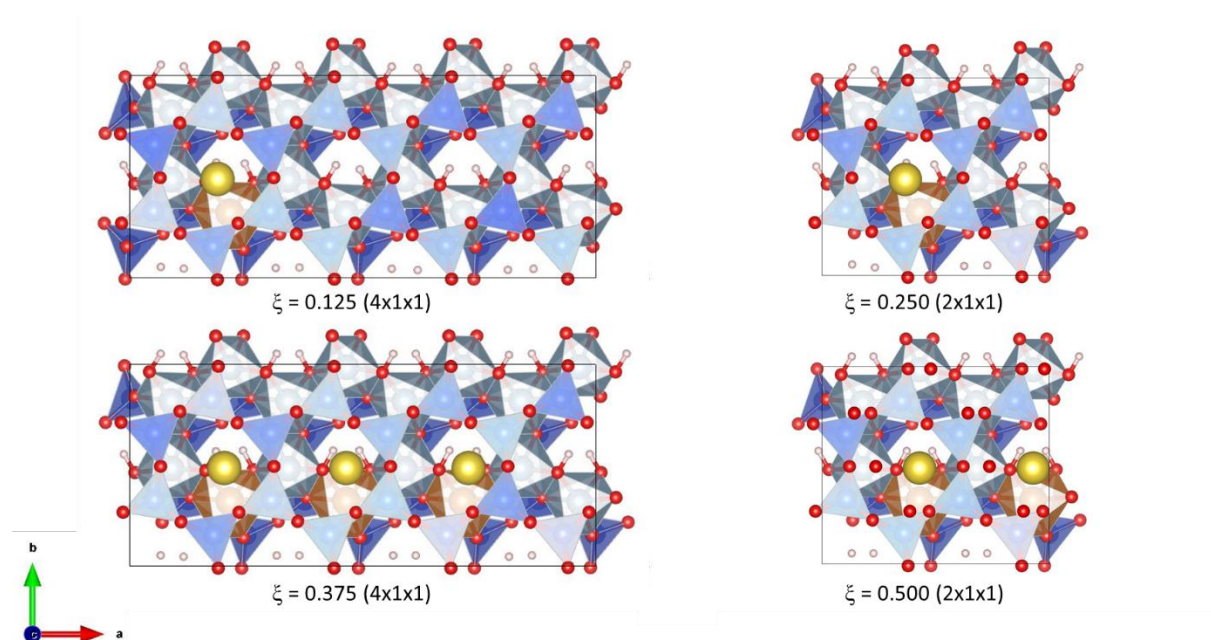


Figure S8. The most stable structure of *cv* Mg_{cis} Na^+ -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

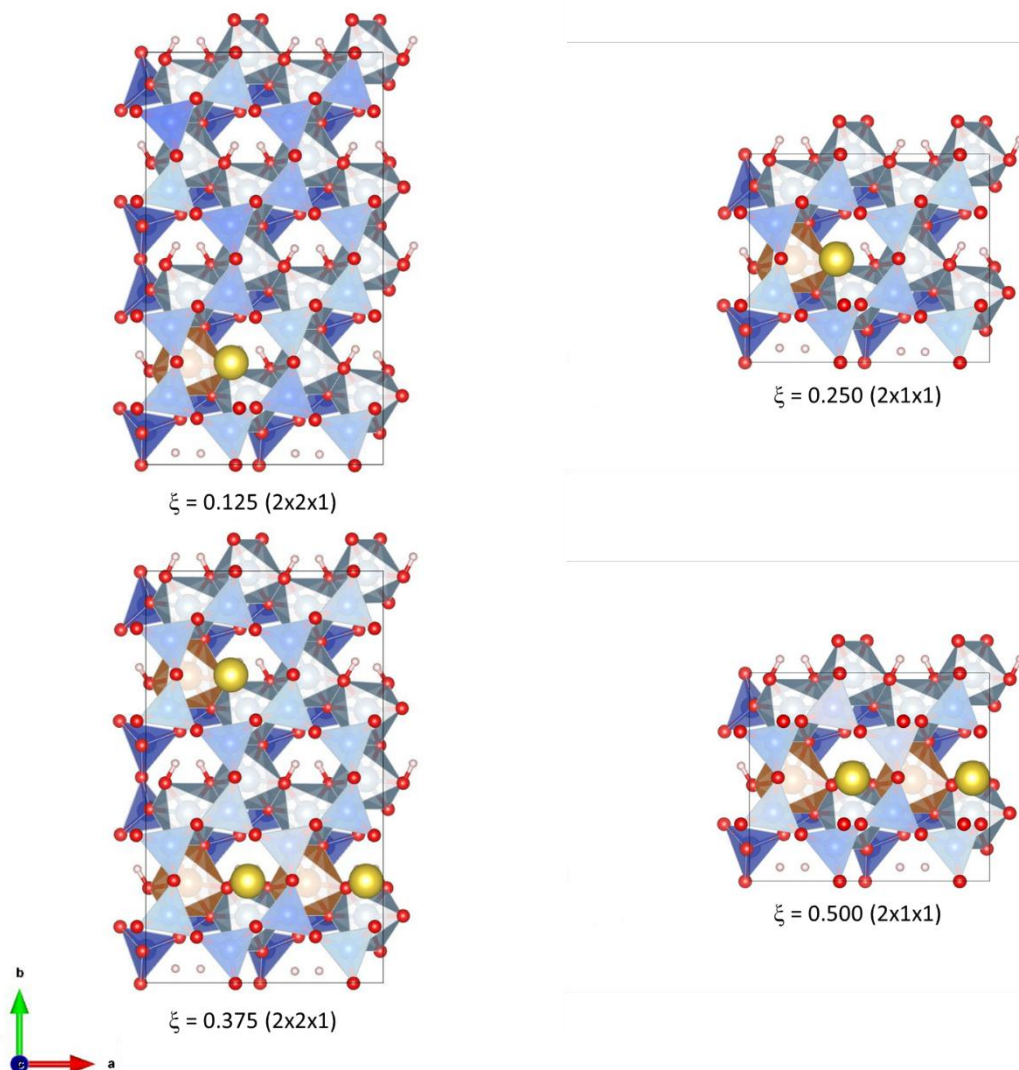


Figure S9. The most stable structure of *cv* Mg_{trans} Na^+ -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

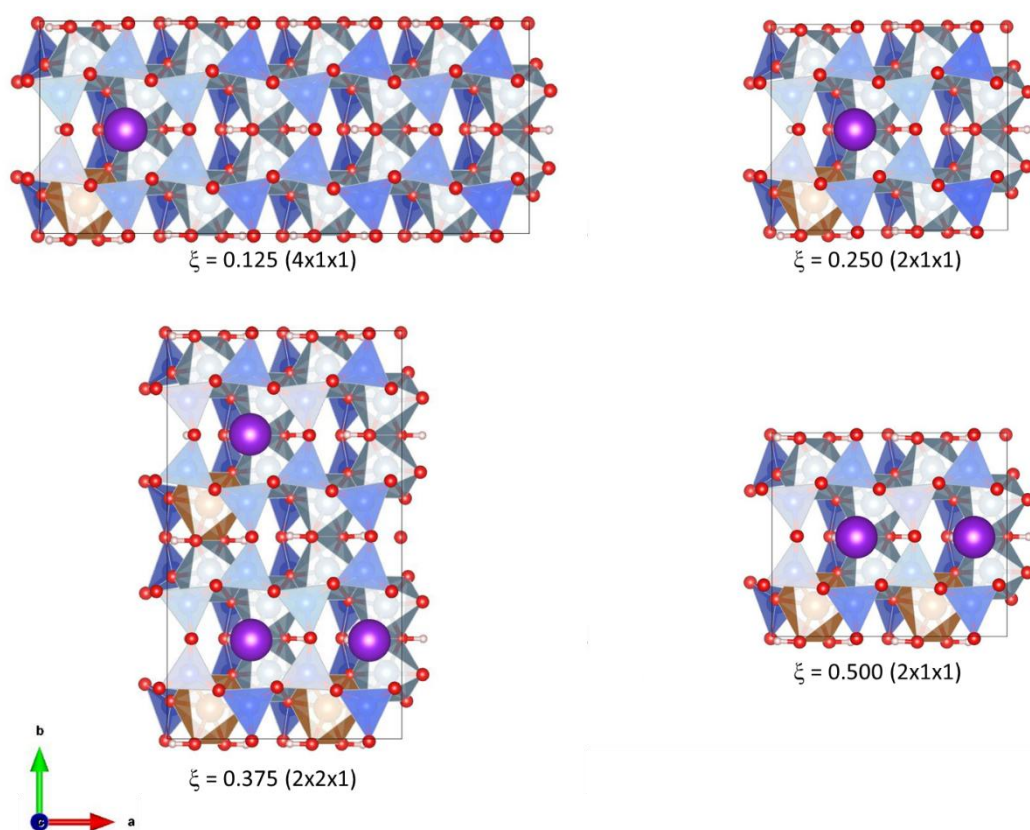


Figure S10. The most stable structure of *tv* Mg_{cis} K⁺-saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

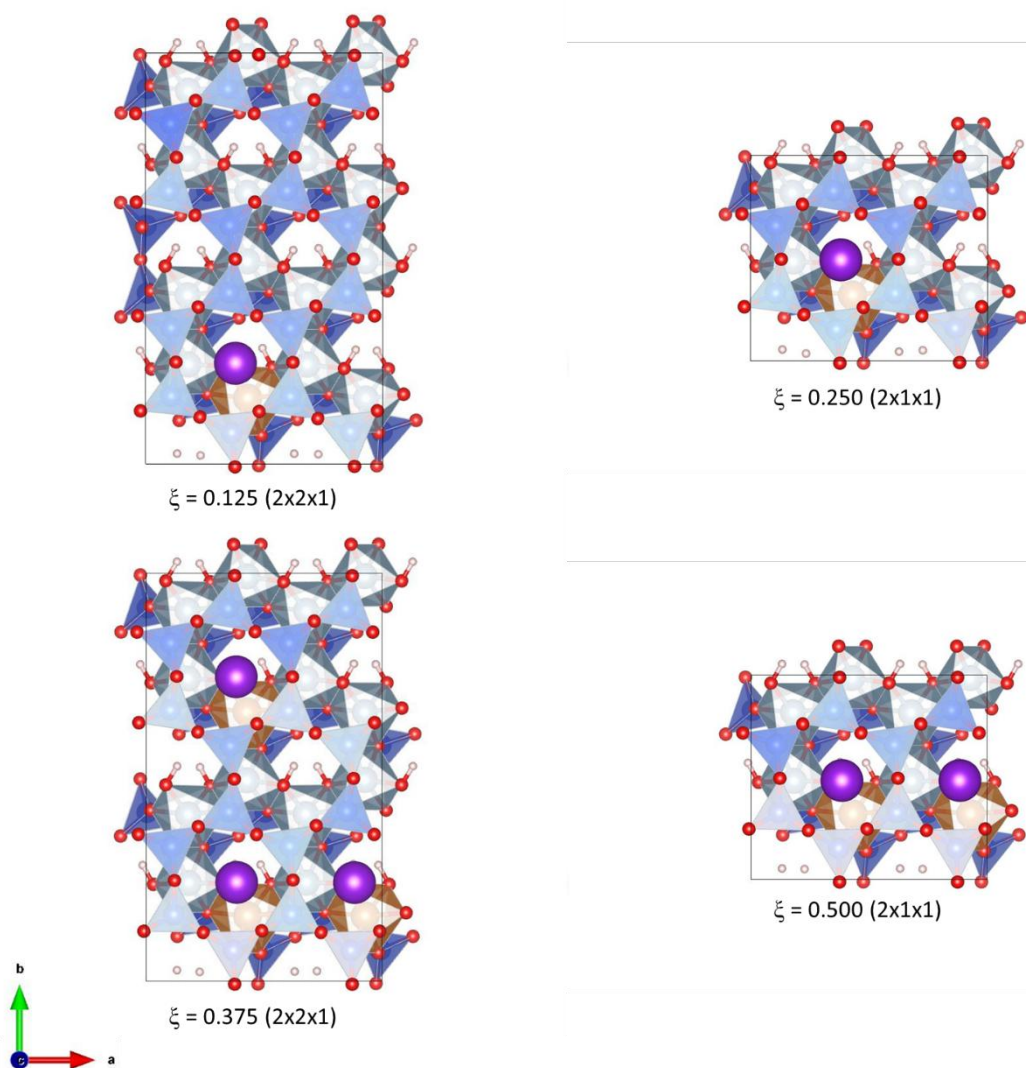


Figure S11. The most stable structure of cv Mg_{cis} K^+ -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

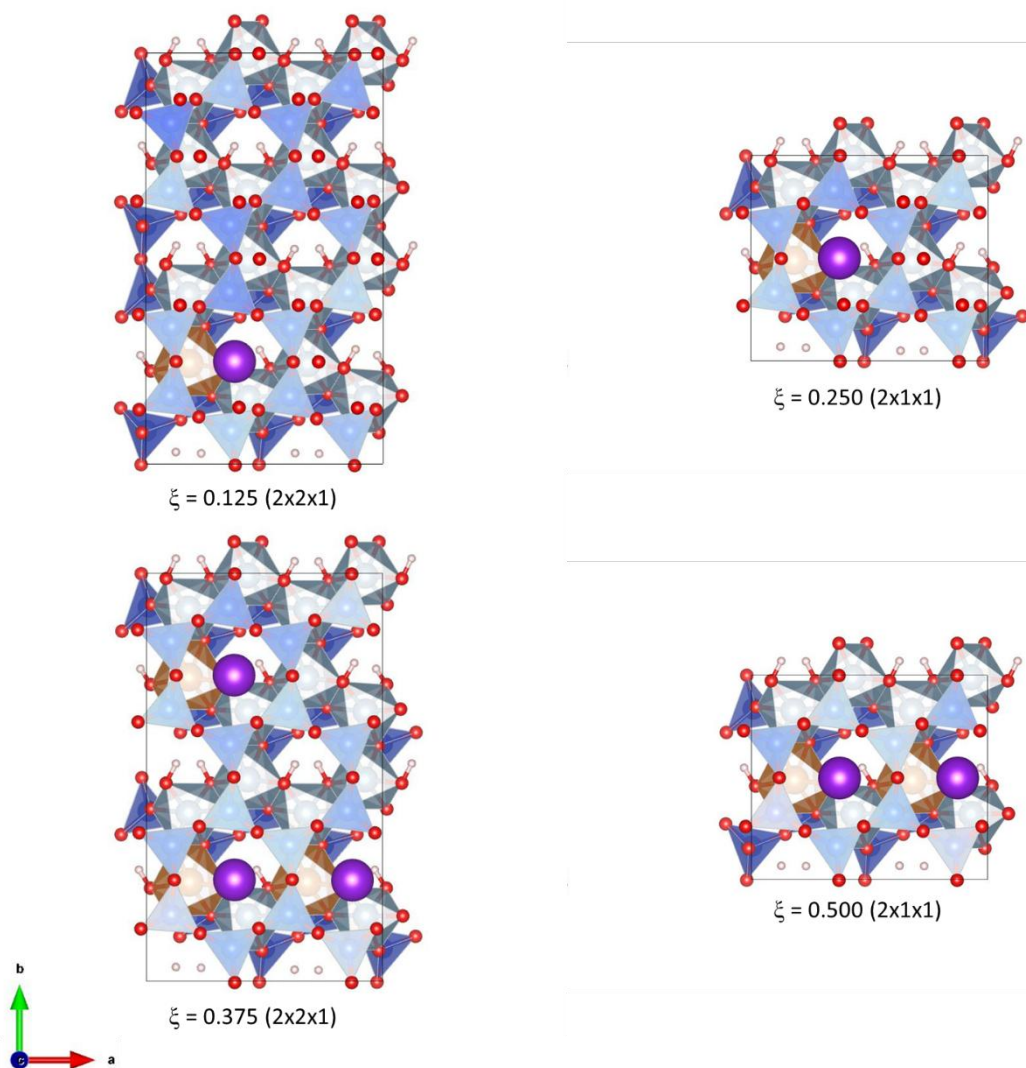


Figure S12. The most stable structure of *cv* Mg_{trans} K^+ -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

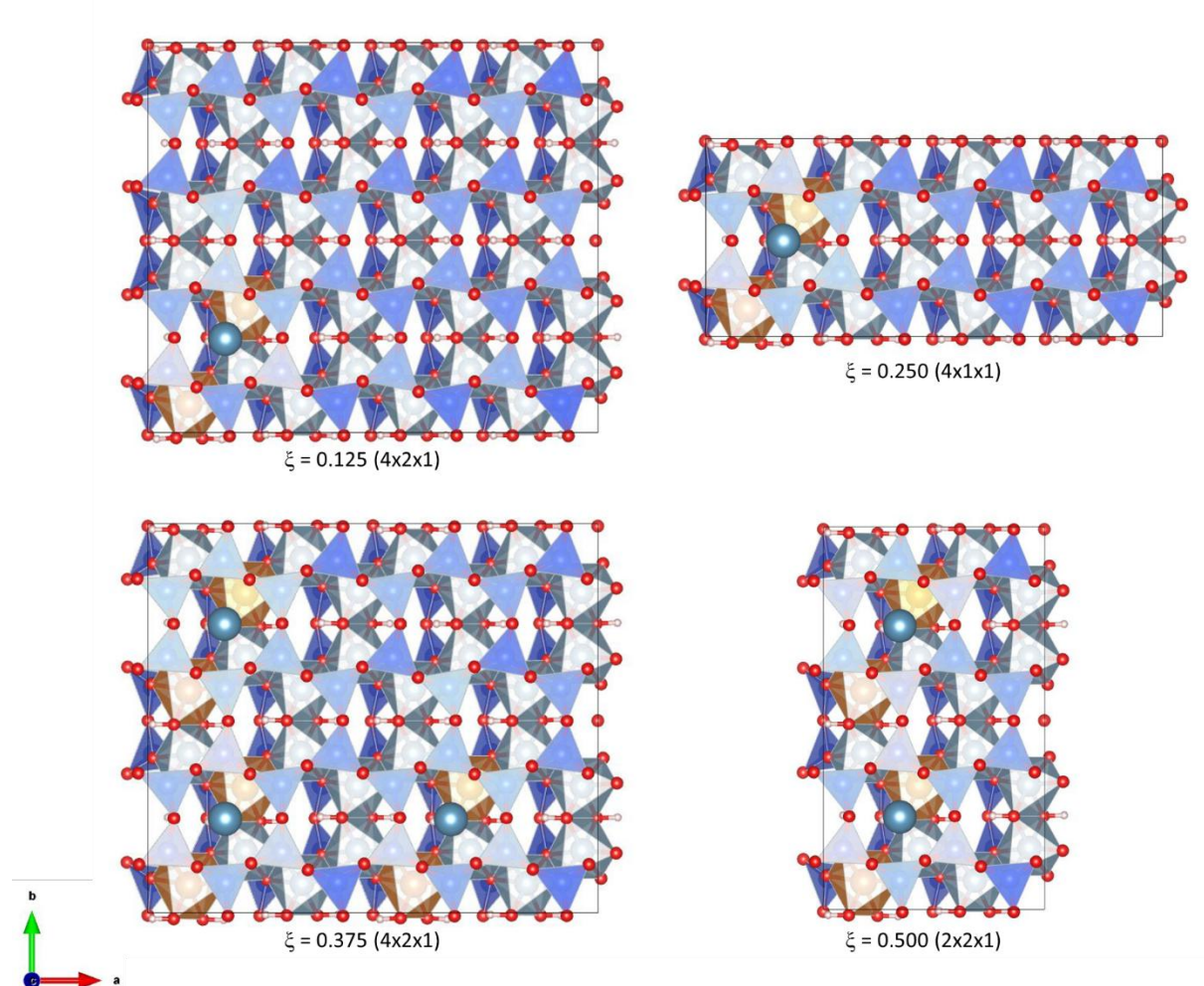


Figure S13. The most stable structure of *tv* Mg_{cis} Ca²⁺-saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

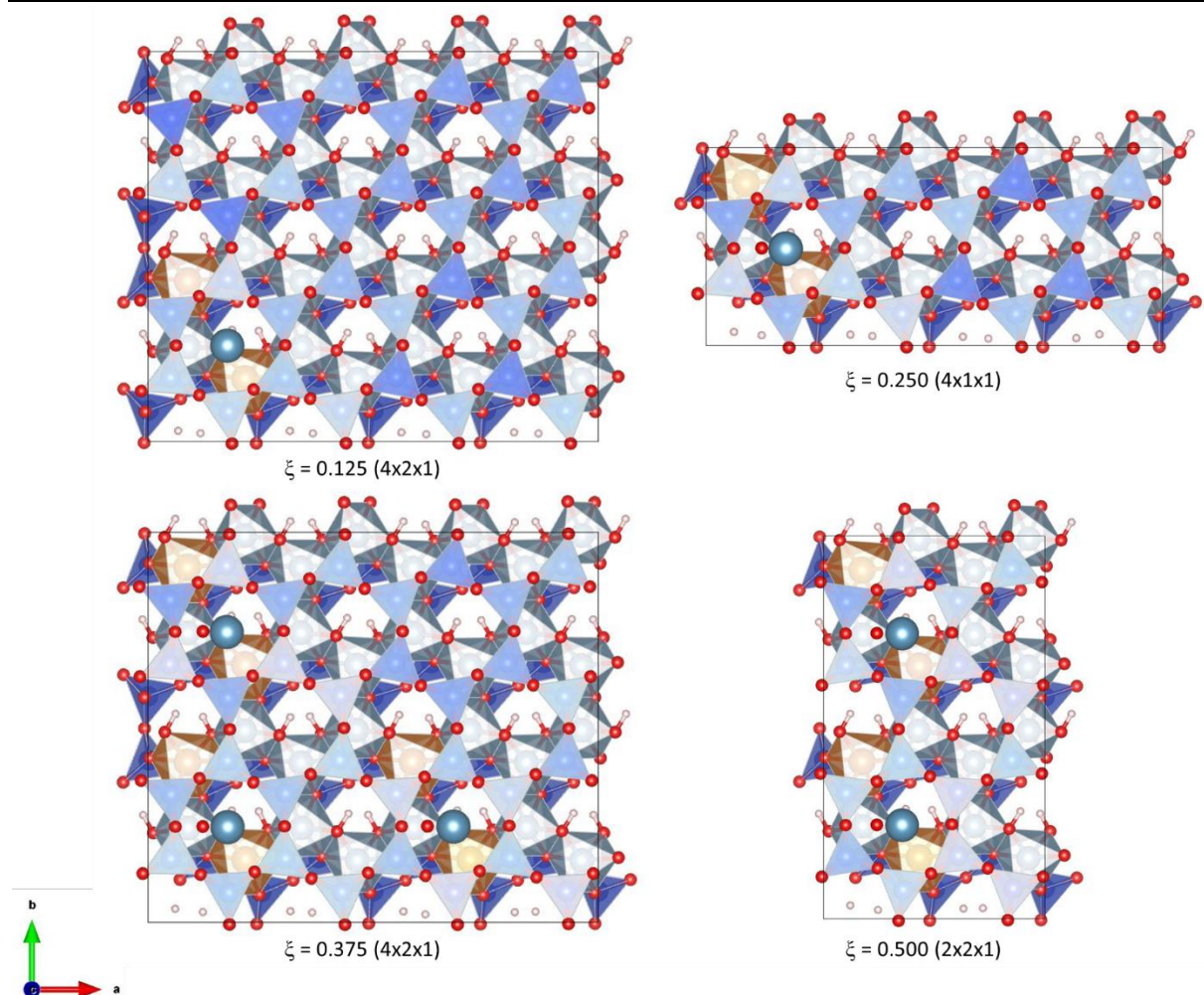


Figure S14. The most stable structure of *cv* Mg_{cis} Ca^{2+} -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

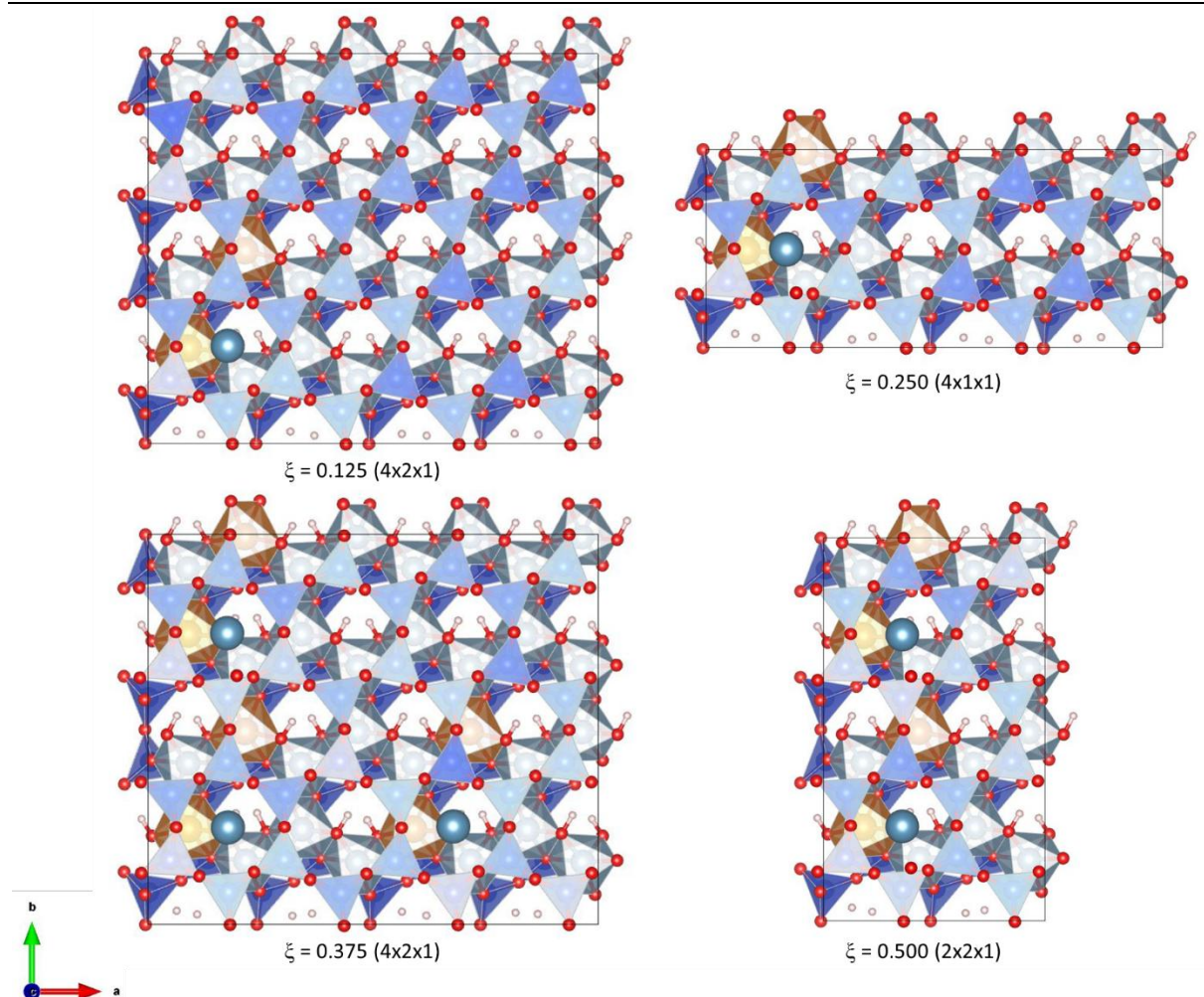


Figure S15. The most stable structure of *cv* Mg_{trans} Ca^{2+} -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

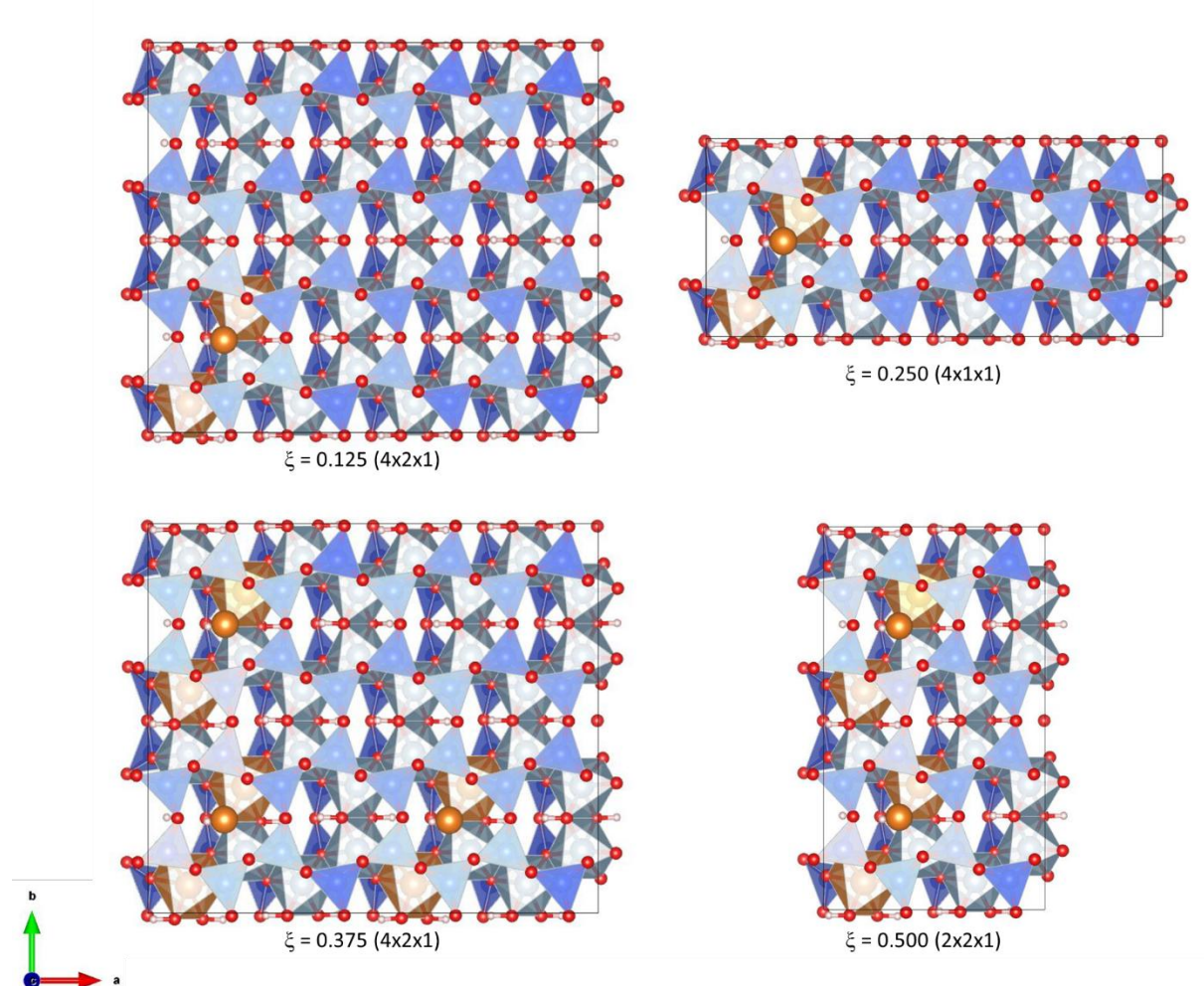


Figure S16. The most stable structure of *tv* Mg_{clis} Mg²⁺-saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

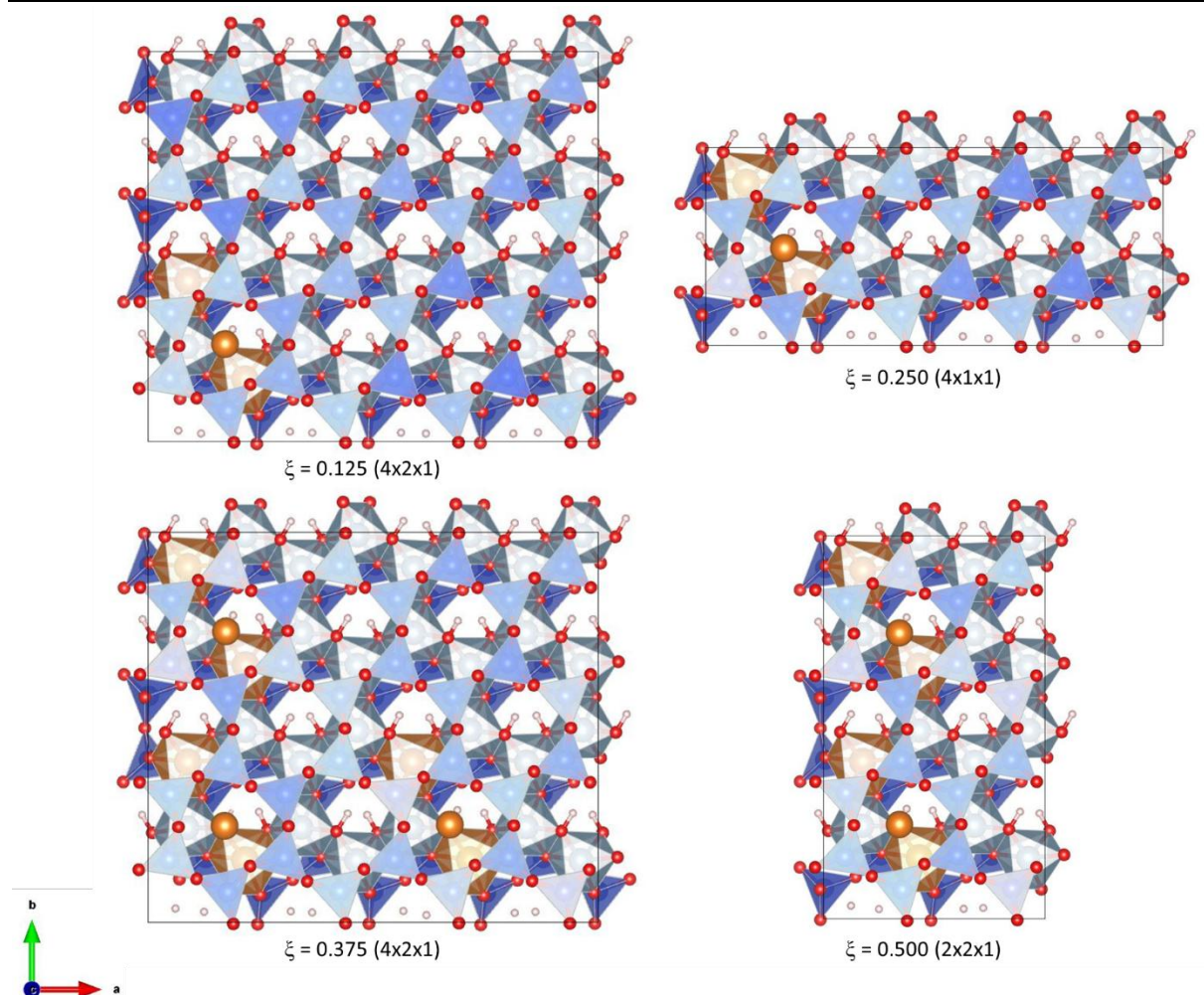


Figure S17. The most stable structure of *cv* Mg_{cis} Mg^{2+} -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

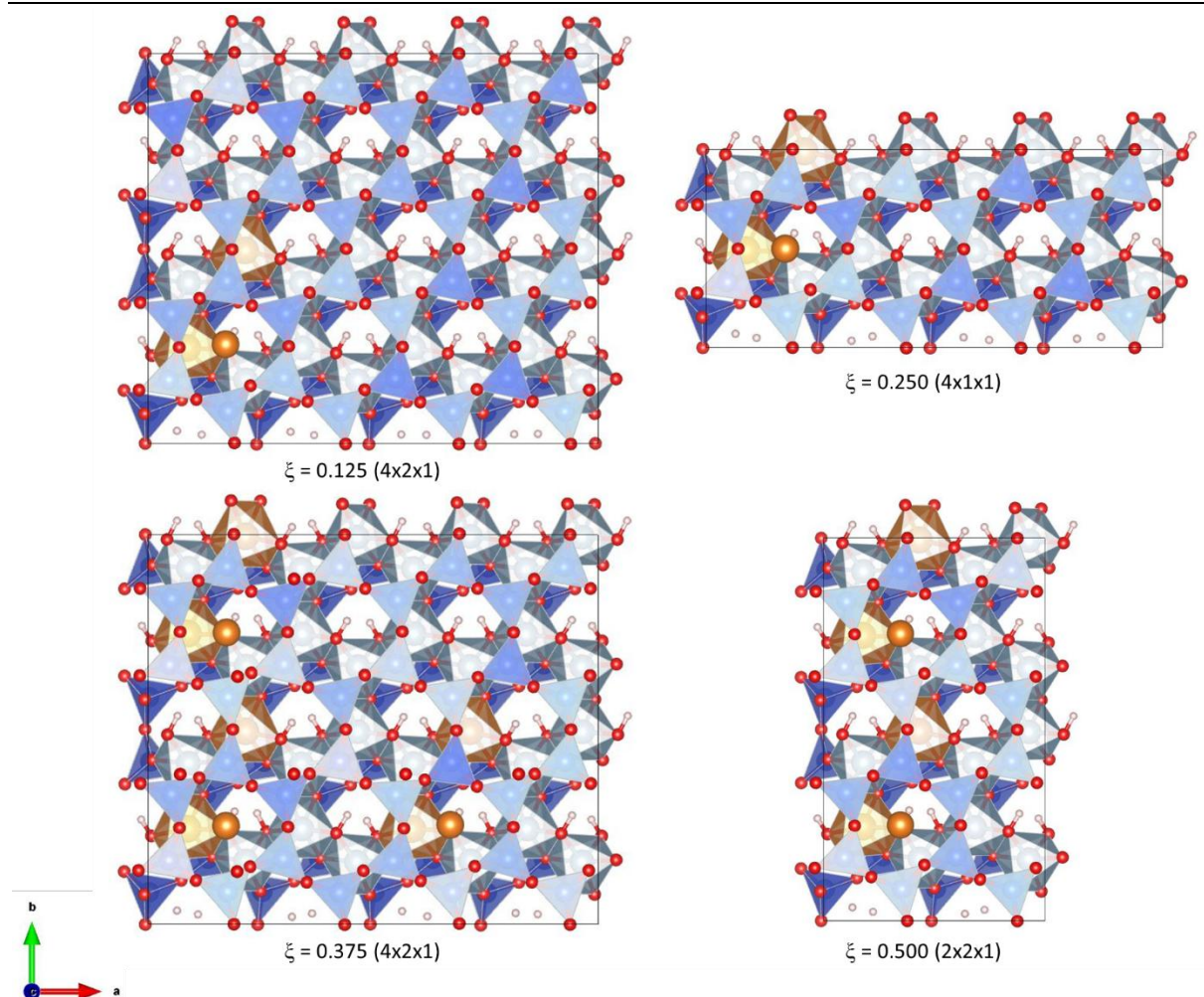


Figure S18. The most stable structure of *cv* Mg_{trans} Mg^{2+} -saturated montmorillonite. White: hydrogen, red: oxygen, blue: silicon, grey: aluminium, orange: magnesium, yellow: sodium and violet: potassium.

Table S14: d_{001} of Na⁺-Montmorillonite

H ₂ O/cation	Layer Charge (ξ) = 0.250			Layer Charge (ξ) = 0.500		
	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}
0	9.73	9.68	9.67	9.74	9.67	9.68
2	11.39	11.43	11.44	11.82	11.81	11.82
4	11.92	11.86	11.93	12.24	12.29	12.28
6	12.09	12.07	12.03	13.54	13.16	13.14
8	12.20	12.39	12.21	14.87	14.98	14.94

Table S15: d_{001} of K⁺-Montmorillonite

H ₂ O/cation	Layer Charge (ξ) = 0.250			Layer Charge (ξ) = 0.500		
	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}
0	10.09	10.02	10.02	10.28	10.16	10.14
2	11.47	11.75	11.69	11.87	12.31	12.20
4	12.13	12.16	12.24	12.80	12.53	12.47
6	12.41	12.26	12.24	13.13	13.25	13.32
8	12.68	12.65	12.60	14.95	14.89	14.99

Table S16: d_{001} of Ca²⁺-Montmorillonite

H ₂ O/cation	Layer Charge (ξ) = 0.250			Layer Charge (ξ) = 0.500		
	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}
0	9.66	9.59	9.59	9.57	9.46	9.48
2	11.39	11.43	11.22	11.66	11.70	11.72
4	11.83	11.82	11.83	11.77	11.86	11.87
6	11.90	11.93	11.96	11.93	11.95	11.94
8	12.31	12.35	12.35	12.16	12.20	12.17

Table S17: d_{001} of Mg²⁺-Montmorillonite

H ₂ O/cation	Layer Charge (ξ) = 0.250			Layer Charge (ξ) = 0.500		
	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}	<i>tv</i> Mg _{cis}	<i>cv</i> Mg _{cis}	<i>cv</i> Mg _{trans}
0	9.67	9.56	9.58	9.57	9.50	9.55
2	10.31	10.25	10.26	10.90	11.00	10.97
4	11.37	11.51	11.42	11.61	11.63	11.63
6	12.10	12.04	12.08	12.06	12.08	12.04
8	12.22	12.19	12.18	12.07	12.14	12.13