The North African Journal of Scientific Publishing (NAJSP)
مجلة شمال إفريقيا للنشر العلمي (NAJSP)
E-ISSN: 2959-4820
Volume 4, Issue 4, 2026
Page No: 246-253
Website: https://najsp.com/index.php/home/index
SJIFactor 2024: 5.49 معامل التأثير العربي (AIF) 2025: 0.69 ISI 2024: 0.696

Interaction of Groundwater-Relevant Ca2+ and Mg2+ with Natural Clay from Derna, Libya: XRF Characterization and Changes in Dissolved Cation Concentrations

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تفاعل أيونات الكالسيوم ***Ca2+*** والمغنيسيوم ***Mg2+*** الموجودة في المياه الجوفية مع الطين الطبيعي من مدينة درنه، ليبيا: التوصيف باستخدام مطيافية الأشعة السينية الفلورية والتغيرات في تركيزات الكاتيونات الذائبة

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Received: August 28, 2026 | Accepted: November 06, 2026 | Published: November 21, 2026

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Abstract:
Calcium and magnesium are the principal divalent cations responsible for most natural-water hardness, and their concentrations may change during contact with clay-rich materials. This study evaluated changes in dissolved Ca^{2+} and Mg^{2+} after short-term contact with a natural green clay from Derna, Libya, using levels derived from local groundwater. The reference sample (GW-6) contained 78 mg/L Ca^{2+} and 31 mg/L Mg^{2+}; Low and High levels were 40/15 and 156/62 mg/L, respectively. XRF characterization with Bruker S2 RANGER and PANalytical MiniPal 4 indicated a bulk composition containing approximately 34 wt.% SiO_2, 9 wt.% Al_2O_3, 5.37 wt.% Fe_2O_3, and 20.8–20.9 wt.% CaO equivalent. Separate Ca-only and Mg-only solutions were contacted with 2.00 g clay in 40.0 mL for 15 min at room temperature and analyzed by EDTA titration. Apparent Ca^{2+} reductions were 6.67%, 4.11%, and 3.45% at Low, Actual, and High levels, while Mg^{2+} reductions were 36.00%, 12.24%, and 8.81%. Because the clay-contact tests were not independently replicated and EDTA does not identify the mechanism responsible for cation loss from solution, the findings are interpreted descriptively as evidence of cation–solid interaction rather than proof of adsorption, ion exchange, or precipitation.

Keywords: Groundwater; calcium; magnesium; natural clay; XRF; EDTA; water hardness; cation–solid interaction.

الملخص:
تُعد أيونات الكالسيوم والمغنيسيوم من أهم الكاتيونات ثنائية التكافؤ المسؤولة عن عسر المياه الطبيعية، وقد تتغير تراكيزهما عند ملامسة المواد الغنية بالطين. هدفت هذه الدراسة إلى تقييم التغير في تراكيز الكالسيوم والمغنيسيوم الذائبة بعد تلامس قصير الأمد مع طين طبيعي أخضر من درنة، ليبيا، باستخدام مستويات مستمدة من كيمياء المياه الجوفية المحلية. احتوت

العينة المرجعية رقم 6 على 78 ملجم/لتر من الكالسيوم و31 ملجم/لتر من المغنيسيوم، بينما حُدد المستوى المنخفض عند 40 و15 ملجم/لتر، والمستوى المرتفع عند 156 و62 ملجم/لتر للكالسيوم والمغنيسيوم، على التوالي. وأظهر توصيف الطين بالأشعة السينية الفلورية أن تركيبه الكيميائي الكلي احتوى تقريبًا على 34% من ثاني أكسيد السيليكون، و9% من أكسيد الألومنيوم، و5.37% من أكسيد الحديد، وما يعادل 20.8–20.9% من أكسيد الكالسيوم. عولجت محاليل منفصلة تحتوي على الكالسيوم فقط أو المغنيسيوم فقط مع 2.00 جم من الطين في 40.0 مل لمدة 15 دقيقة عند درجة حرارة الغرفة، ثم حُللت بالمعايرة المعقدية باستخدام الإديتا. بلغت الانخفاضات الظاهرية في تركيز الكالسيوم 6.67% و4.11% و3.45% عند المستويات المنخفض والفعلي والمرتفع، على التوالي، بينما بلغت في المغنيسيوم 36.00% و12.24% و8.81%. ونظرًا لعدم تكرار تجارب التلامس مع الطين بصورة مستقلة ولأن معايرة الإديتا لا تحدد آلية فقدان الكاتيونات من المحلول، فُسرت النتائج وصفيًا باعتبارها دليلًا على تفاعل الكاتيونات مع المادة الصلبة، وليس إثباتًا للامتزاز أو التبادل الأيوني أو الترسيب.

الكلمات المفتاحية: المياه الجوفية؛ الكالسيوم؛ المغنيسيوم؛ الطين الطبيعي؛ تقنية XRF؛ تقنية EDTA؛ عسر الماء؛ التفاعل بين الكاتيونات والمادة الصلبة.

Introduction:

Calcium and magnesium are the principal dissolved divalent cations associated with water hardness. Their concentrations influence scaling behavior, treatment requirements, and the chemical response of water during domestic and industrial use. Standard analytical practice therefore treats Ca^{2+} and Mg^{2+} as core hardness constituents, and complexometric titration remains an established approach for their determination in water [1, 2, 3]. Recent work continues to emphasize that Ca^{2+} and Mg^{2+} do not behave identically during softening or precipitation, so interpreting them separately can be important when evaluating water–solid interactions [4].

Natural clays are attractive low-cost materials for water treatment because their bulk chemistry, surface charge, exchangeable cations, porosity, and mineral structure can provide sites for interactions with dissolved species. However, these properties vary widely among natural deposits, and bulk composition alone does not determine performance. Reviews of clay-based treatment systems emphasize the combined importance of mineralogy, cation-exchange capacity, surface area, pH, ionic strength, and solution chemistry [5, 6]. Consequently, a natural clay collected from a specific locality should be characterized and evaluated under experimentally defined conditions rather than assumed to behave like a purified reference clay.

Ca^{2+} and Mg^{2+} can interact with aluminosilicate and other mineral surfaces through several pathways, including ion exchange, electrostatic association, and, depending on pH and mineral chemistry, precipitation or dissolution-related processes. Classical exchange studies on bentonite and montmorillonite demonstrate that Ca–Mg selectivity depends on clay structure and solution composition [7, 8]. More recent groundwater studies also show that cation exchange with clay-bearing sediments can alter Ca and Mg concentrations during water–rock interaction. These observations support the plausibility of cation–solid interaction, but they also show why a concentration decrease alone cannot identify a unique mechanism.

From a treatment perspective, several mineral materials have been evaluated for hardness control. Natural zeolite has been used to reduce Ca^{2+}, Mg^{2+}, and total hardness in groundwater [9], while natural and modified pumice have shown measurable Ca^{2+} and Mg^{2+} uptake in controlled aqueous systems [10]. A recent bentonite study likewise reported substantial hardness removal under optimized experimental conditions and emphasized the role of clay composition and surface properties [11]. These studies provide useful context, but their materials, doses, contact times, pH conditions, and mechanistic evidence differ substantially from those available for the natural Derna clay.

The present study was designed around a narrower question. Rather than attempting to establish a complete water-softening process or adsorption mechanism, we asked whether dissolved Ca^{2+} and Mg^{2+} concentrations, selected from local groundwater measurements, change after short-term contact with a natural clay from Derna, Libya. Groundwater data from six samples were used to define environmentally relevant test levels. The selected clay was characterized by XRF to provide bulk chemical context, and standardized EDTA complexometric titration was used to quantify Ca^{2+} and Mg^{2+} before and after clay contact. Because the clay-contact experiments were not independently replicated, all changes are treated descriptively, and no inferential statistical significance is claimed.

Materials and Methods:

1. **Groundwater chemistry and selection of Ca^{2+}/Mg^{2+} levels:** Physicochemical data from six groundwater samples from the Derna study area were reviewed to establish a field-based concentration context. The available laboratory reports included pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium hardness, magnesium hardness, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and NO_3^{-}. Because some original handwritten well names were not reliably legible, the samples were retained as GW-1 to GW-6. EC values are reported in µS/cm as confirmed by the analytical laboratory. GW-6 was selected as the reference sample and contained 78 mg/L Ca^{2+} and 31 mg/L Mg^{2+}. These values defined the Actual condition. Low concentrations were set at approximately half of the reference values using practical rounded concentrations (40 mg/L Ca^{2+} and 15 mg/L Mg^{2+}), while High concentrations were set at twice the reference values (156 mg/L Ca^{2+} and 62 mg/L Mg^{2+}). The test solutions therefore represented groundwater-relevant Ca^{2+} and Mg^{2+} concentrations rather than a full synthetic reconstruction of the groundwater matrix.
2. **Natural clay and XRF characterization:** The solid used in the cation-contact tests was the selected natural green clay (Clay 5) collected from Derna, Libya. Bulk chemical composition was characterized using two benchtop XRF instruments available at a local cement-testing facility: a Bruker S2 RANGER and a PANalytical MiniPal 4. Instrument outputs were documented from display photographs because raw digital exports were not available. The Bruker output reported oxide-equivalent concentrations directly, whereas the PANalytical output reported Ca and Mg primarily as $CaCO_3$ and $MgCO_3$ and also displayed corresponding CaO and MgO values. For comparison, carbonate-reported Ca and Mg were converted stoichiometrically to oxide equivalents. The two instrument results were treated as a cross-instrument comparison, not as analytical replicates, and discrepant values were retained rather than averaged. XRF was used only to describe bulk chemical composition. No mineral phase was assigned because X-ray diffraction (XRD) was not available.
3. **Reagents and EDTA standardization:** Calcium and magnesium were quantified by EDTA complexometric titration following the general analytical basis of ASTM D511-14(2021) e1 [1] and ISO 6058/6059 [2, 3]. An anhydrous $CaCO_3$ primary standard was prepared by accurately weighing 0.1251 g $CaCO_3$, dissolving it with diluted HCl (1:1), expelling residual CO_2 by gentle heating, cooling, transferring quantitatively to a 250 mL volumetric flask, and diluting to volume with distilled water. The calculated calcium-standard concentration was 0.0049997 mol/L (approximately 0.005000 mol/L). A 20.00 mL aliquot was titrated with EDTA in triplicate. EDTA volumes were 18.70, 18.70, and 18.80 mL, corresponding to a mean standardized EDTA concentration of 0.005338 mol/L (reported operationally as 0.00534 mol/L). The mean titration volume was 18.733 mL, with SD 0.058 mL and RSD 0.31%. This precision assessment applies only to EDTA standardization and not to the subsequent clay-contact experiments.
4. **Clay–cation contact experiments:** Calcium and magnesium were investigated in separate single-cation systems. For each condition, 2.00 g of the natural clay was contacted with 40.0 mL of the relevant cation solution for 15 min at room temperature. After contact, the suspension was filtered. A 20.00 mL aliquot of the filtrate was used for EDTA titration. Corresponding cation solutions that had not contacted clay were titrated as the before-contact measurements. Target Ca^{2+} concentrations were 40, 78, and 156 mg/L, and target Mg^{2+} concentrations were 15, 31, and 62 mg/L.
5. **Calcium and magnesium titration procedures:** For Ca^{2+} determination, a 20.00 mL aliquot was rendered strongly alkaline with 1 mol/L NaOH to approximately pH 12–13. A consistent amount of murexide/NaCl indicator mixture was added, and the sample was titrated with standardized EDTA to a stable pink/salmon-to-purple/violet endpoint. For Mg^{2+} determination, a 20.00 mL aliquot of the Mg-only solution was buffered to approximately pH 10 using NH_4Cl/NH_3 buffer, followed by addition of Eriochrome Black T/NaCl indicator. The sample was titrated to the characteristic wine-red/reddish-to-blue endpoint. Because the magnesium test solutions contained Mg^{2+} without added Ca^{2+}, EDTA consumption was used directly to calculate Mg^{2+} concentration.
6. **Blank checks and calculations** Distilled-water controls were evaluated under the calcium and magnesium procedures before and after clay contact. No detectable Ca^{2+}- or Mg^{2+}-attributable titration response was observed. These checks support the absence of a measurable cation contribution from the distilled-water blank under the applied titrimetric conditions, but they do not replace matrix-matched blanks or instrumental speciation measurements.

Cation concentration was calculated from the 1:1 metal–EDTA stoichiometry using:

$$C_{cation}\ (mg/L) = [M_{EDTA} \times V_{EDTA}\ (L) \times MW_{cation} \times 1000] / V_{sample}\ (L)$$

Where V_{sample} = 0.02000 L, MW_{Ca} = 40.078 g/mol, and MW_{Mg} = 24.305 g/mol.

The apparent decrease in dissolved concentration and apparent reduction were calculated **as:**

$$\text{Apparent decrease (mg/L)} = C_{before} - C_{after}$$

$$\text{Apparent reduction (\%)} = [(C_{before} - C_{after}) / C_{before}] \times 100$$

An apparent solid-associated amount was also calculated descriptively **as:**

$$\text{Apparent solid-associated amount (mg/g)} = [(C_{before} - C_{after}) \times V_{solution}\ (L)] / m_{clay}\ (g)$$

This last quantity represents loss from the dissolved phase normalized to clay mass; it is not interpreted as proof of a specific adsorption mechanism.

7. **Data analysis and statistical scope:** The EDTA clay-contact experiments were not independently replicated. Accordingly, the before/after measurements, concentration changes, apparent reductions, and apparent solid-associated amounts were evaluated descriptively only. No inferential statistical testing, confidence intervals, or significance claims were applied to the clay-contact results. The triplicate EDTA standardization measurements were used solely to assess titrant standardization precision.

Results:

1. **Groundwater hydrochemical context:** The six groundwater samples showed clear hydrochemical variability. pH ranged from 7.08 to 8.29, TDS from 588 to 1880 mg/L, total hardness from 145 to 380 mg/L as $CaCO_3$, Ca^{2+} from 36 to 78 mg/L, and Mg^{2+} from 12 to 33 mg/L. GW-6 had the highest measured Ca^{2+} concentration (78 mg/L), the highest TDS (1880 mg/L), and the highest total hardness (380 mg/L as $CaCO_3$) among the six samples; its corrected Mg^{2+} concentration was 31 mg/L. These Ca^{2+} and Mg^{2+} values formed the Actual test condition, with Low and High levels derived around them.

Table (1): Selected hydrochemical characteristics of the six groundwater samples.

Sample	pH	EC (µS/cm)	TDS (mg/L)	TH (mg/L as $CaCO_3$)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
GW-1	7.08	1224	588	206	50	20
GW-2	8.14	2924	1300	324	75	33
GW-3	7.24	1911	920	200	54	16
GW-4	7.10	1310	610	145	36	13
GW-5	7.09	1510	700	216	66	12
GW-6 (reference)	8.29	2420	1880	380	78	31

2. **Bulk chemical composition of the natural clay:** Both XRF datasets indicated a silica-rich, alumina-bearing, Ca-rich bulk composition. SiO_2 was approximately 33.6–34.7 wt.%, Al_2O_3 approximately 8.8–9.6 wt.%, Fe_2O_3 approximately 5.37 wt.%, and the calcium-bearing fraction approximately 20.8–20.9 wt.% as CaO equivalent. Agreement was particularly close for Fe_2O_3 and CaO and was reasonably close for SiO_2, Al_2O_3, and TiO_2. Larger differences were present for MgO, SO_3, and K_2O. Because the instruments may differ in calibration libraries, matrix corrections, and reporting conventions, these differences were retained rather than averaged.

Table (2): Selected XRF results for the natural Derna clay.

Component	Bruker S2 RANGER (wt.%)	PANalytical MiniPal 4 / harmonized (wt.%)	Interpretive note
SiO_2	34.722	33.645	Close agreement
Al_2O_3	9.552	8.814	Broadly similar
Fe_2O_3	5.373	5.377	Very close agreement
CaO	20.915	20.840 displayed (20.807 stoichiometric)	Very close agreement
MgO	2.035	1.386	Larger difference
SO_3	8.135	1.326	Large difference
Na_2O	0.597	0.469	Moderate difference
K_2O	0.260	0.709	Large relative difference
TiO_2	0.797	0.859	Close agreement

3. **EDTA standardization:** The $CaCO_3$-derived standard was 0.0049997 mol/L. Titration of three 20.00 mL aliquots required 18.70, 18.70, and 18.80 mL EDTA. The corresponding EDTA molarities were 0.005347, 0.005347, and 0.005319 mol/L, giving a mean of 0.005338 mol/L. The titration-volume RSD was 0.31%, indicating good repeatability of the EDTA standardization step.

Table (3): EDTA standardization using the $CaCO_3$-derived calcium standard.

Replicate	EDTA volume (mL)	Calculated EDTA molarity (mol/L)
1	18.70	0.005347
2	18.70	0.005347
3	18.80	0.005319
Mean	18.733	0.005338

4. **Changes in dissolved Ca^{2+} after clay contact:** Measured Ca^{2+} concentrations before clay contact were 40.11, 78.08, and 155.10 mg/L for the Low, Actual, and High levels, respectively, closely matching the target concentrations. After 15 min clay contact, the corresponding concentrations were 37.44, 74.87, and 149.75 mg/L. The absolute decreases were 2.67, 3.21, and 5.35 mg/L, corresponding to apparent reductions of 6.67%, 4.11%, and 3.45%. Apparent solid-associated amounts were 0.053, 0.064, and 0.107 mg/g, respectively.

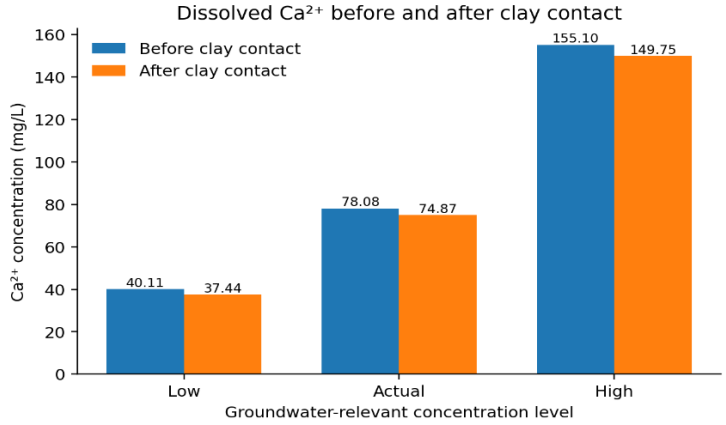


Fig (1): Measured dissolved Ca^{2+} concentrations before and after 15 min contact with the natural clay. No error bars are shown because the clay-contact conditions were not independently replicated.

5. **Changes in dissolved Mg^{2+} after clay contact:** Measured Mg^{2+} concentrations before clay contact were 16.22, 31.78, and 62.60 mg/L for the Low, Actual, and High levels, respectively. After clay contact, concentrations were 10.38, 27.89, and 57.08 mg/L. The absolute decreases were 5.84, 3.89, and 5.51 mg/L, corresponding to apparent reductions of 36.00%, 12.24%, and 8.81%. Apparent solid-associated amounts were 0.117, 0.078, and 0.110 mg/g, respectively.

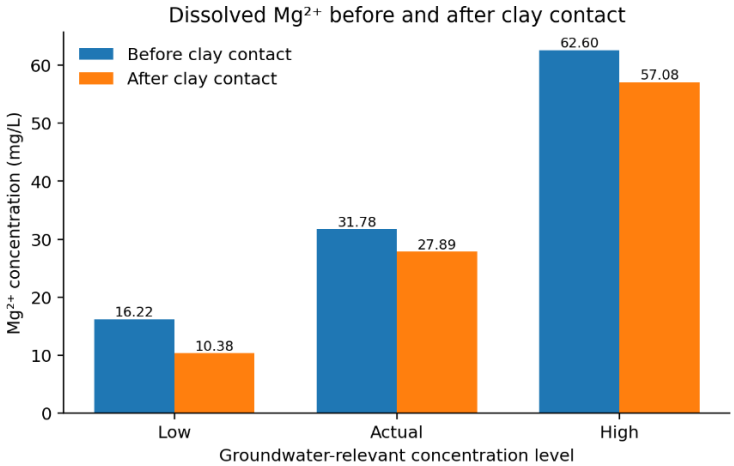


Fig (2): Measured dissolved Mg^{2+} concentrations before and after 15 min contact with the natural clay. No error bars are shown because the clay-contact conditions were not independently replicated.

6. Integrated Ca^{2+}/Mg^{2+} clay-contact results:

Table (4): Raw EDTA volumes and derived descriptive results for the controlled single-cation clay-contact experiments.

Cation	Level	Target (mg/L)	EDTA before (mL)	EDTA after (mL)	Measured before (mg/L)	Measured after (mg/L)	Apparent reduction (%)	Apparent amount (mg/g)
Ca^{2+}	Low	40	3.75	3.50	40.11	37.44	6.67	0.053
Ca^{2+}	Actual	78	7.30	7.00	78.08	74.87	4.11	0.064
Ca^{2+}	High	156	14.50	14.00	155.10	149.75	3.45	0.107
Mg^{2+}	Low	15	2.50	1.60	16.22	10.38	36.00	0.117
Mg^{2+}	Actual	31	4.90	4.30	31.78	27.89	12.24	0.078
Mg^{2+}	High	62	9.65	8.80	62.60	57.08	8.81	0.110

Across the three levels, the relative decrease was consistently larger for Mg^{2+} than for Ca^{2+}. However, because each clay-contact condition represents a single experiment, these differences are descriptive and cannot be used to establish statistical superiority, selectivity, or a specific removal mechanism.

Discussion:

1. **Groundwater-referenced design:** A central feature of this study is that the tested Ca^{2+} and Mg^{2+} levels were anchored to measured groundwater chemistry rather than selected solely for laboratory convenience. The six-well dataset showed that Ca^{2+} and Mg^{2+} varied substantially across the study area, while GW-6 provided a high-hardness reference containing 78 mg/L Ca^{2+} and 31 mg/L Mg^{2+}. Using approximately half, actual, and double values created a controlled concentration range around a real local reference point. This does not make the test solutions equivalent to natural groundwater because Na^{+}, Cl^{-}, SO_4^{2-}, alkalinity, dissolved organic matter, and other constituents were not reproduced. Instead, the design isolates short-term Ca^{2+}/Mg^{2+} behavior while preserving a direct link to local hydrochemistry.
2. **Meaning of the observed Ca^{2+} decrease:** Ca^{2+} decreased after clay contact at all three tested levels, but the relative reduction declined from 6.67% at Low to 4.11% at Actual and 3.45% at High. The absolute decrease increased with starting concentration, from 2.67 to 5.35 mg/L, whereas the percentage change became smaller. This pattern can arise when the number or accessibility of reactive sites is limited relative to the amount of dissolved solute, although the present dataset does not establish site saturation or an adsorption isotherm. Mineral-based hardness-removal studies show that Ca^{2+} can interact strongly with aluminosilicate and other mineral surfaces, but reported capacities and mechanisms vary with pH, mineral phase, cation-exchange capacity, and contact time [9, 10, 11]. Our 15 min, unmodified-clay experiment was intentionally simpler and should not be compared directly with optimized softening systems.
3. **Meaning of the observed Mg^{2+} decrease:** Mg^{2+} also decreased at all three levels and showed larger relative changes than Ca^{2+}: 36.00%, 12.24%, and 8.81% at Low, Actual, and High, respectively. The strongest relative change occurred at the lowest Mg^{2+} concentration, while the apparent solid-associated amounts remained within a relatively narrow range of 0.078–0.117 mg/g. These observations are compatible with concentration-dependent cation–solid interaction, but they do not establish preferential Mg^{2+} adsorption. Classical Ca–Mg exchange studies show that selectivity can vary with clay mineralogy and electrolyte background, and in some bentonite systems a slight preference for Ca^{2+} over Mg^{2+} has been reported [7, 8]. The present natural clay is chemically heterogeneous and not mineralogically resolved, so the larger Mg^{2+} percentage decrease cannot be assigned to a specific exchange preference.
4. **XRF composition as chemical context, not mechanism:** The XRF results show that the Derna clay contains substantial Si-, Al-, Fe-, and Ca-bearing fractions. Such a composition is consistent with a natural geological material capable of providing multiple types of surface and exchange environments. However, XRF measures bulk elemental/oxide composition and cannot identify the crystalline phases in which those elements occur. Similarly, the high CaO-equivalent signal cannot be taken as evidence that a particular calcium mineral controlled the cation-contact response. Recent reviews emphasize that clay performance depends not only on bulk chemistry but also on mineral structure, cation-exchange capacity, surface area, porosity, pH-dependent charge, and solution chemistry [5, 6]. Because XRD, BET surface area, CEC, zeta potential, and point of zero

charge were not available, the XRF data are appropriately used here as compositional context rather than as proof of an ion-exchange or adsorption pathway.

5. **Possible pathways and why they remain unresolved:** A decrease in dissolved Ca^{2+} or Mg^{2+} after clay contact can result from more than one process. Cation exchange with pre-existing surface or interlayer ions is plausible for clay-bearing materials; electrostatic surface association can also contribute. Depending on local pH, carbonate availability, and the identity of mineral phases, dissolution–precipitation processes may further modify dissolved concentrations. These pathways cannot be distinguished by EDTA titration alone. EDTA quantifies the dissolved divalent cation remaining in the aliquot under the titration conditions, but it does not identify where the missing cation resides or whether it is exchange-bound, surface-associated, incorporated into a precipitate, or otherwise removed from the measured aqueous phase. For this reason, the terms apparent reduction and cation–solid interaction are used throughout the manuscript.
6. **Relation to existing hardness-removal studies:** The magnitude of the changes observed here is lower than the optimized removal efficiencies reported for engineered or highly characterized hardness-removal materials. Hailu et al. [9] evaluated natural zeolite for groundwater Ca^{2+} and Mg^{2+} removal, while Sepehr et al. [10] reported considerably higher uptake using pumice, particularly after alkaline modification. Mostafa et al. [11] reported high total-hardness removal using bentonite under optimized conditions involving controlled pH, dose, concentration, and contact time. These studies demonstrate that mineral solids can be effective hardness-control materials, but they also underscore the importance of experimental conditions and material identity. The contribution of the present work is more limited and local: it establishes that a natural Derna clay measurably altered dissolved Ca^{2+} and Mg^{2+} concentrations over 15 min at concentrations derived from local groundwater, while documenting the bulk chemistry of the material and preserving uncertainty about mechanism.

Limitations:

- The Ca^{2+} and Mg^{2+} clay-contact conditions were not independently replicated; therefore, the reported concentration changes and apparent reductions are descriptive and cannot support inferential statistical claims.
- The study used one clay mass (2.00 g), one solution volume (40.0 mL), one contact time (15 min), and room-temperature conditions. It therefore does not define kinetics, equilibrium isotherms, thermodynamics, maximum capacity, or process optimization.
- Only separate single-cation Ca^{2+} and Mg^{2+} systems were tested. Competition between Ca^{2+} and Mg^{2+}, and interactions with Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, alkalinity, and other groundwater constituents, were not evaluated in this experiment.
- EDTA complexometric titration quantifies dissolved cations but does not identify the process responsible for a decrease after clay contact. Adsorption, ion exchange, precipitation, surface association, or combinations of processes therefore cannot be distinguished.
- XRF provided bulk chemical composition but XRD mineral-phase identification was unavailable. BET surface area, cation-exchange capacity, zeta potential, pHpzc, pore-size distribution, and post-contact solid characterization were also unavailable.
- The XRF results were transcribed from instrument displays. Raw spectra, calibration certificates, replicate XRF analyses, certified reference-material checks, and complete sample-preparation records were not available. The two XRF instruments therefore provide a descriptive cross-instrument comparison rather than formal analytical validation.
- The groundwater-derived test solutions reproduced selected Ca^{2+} and Mg^{2+} concentrations only and should not be interpreted as complete synthetic groundwater.

Conclusions:

This study evaluated short-term changes in dissolved Ca^{2+} and Mg^{2+} after contact with a natural green clay from Derna, Libya, using concentration levels derived from local groundwater chemistry. Groundwater sample GW-6, containing 78 mg/L Ca^{2+} and 31 mg/L Mg^{2+}, defined the Actual level, while approximately half and double concentrations defined the Low and High conditions. XRF characterized the clay as a silica-rich, alumina-bearing, Ca-rich natural material with approximately 34 wt.% SiO_2, 9 wt.% Al_2O_3, 5.37 wt.% Fe_2O_3, and 20.8–20.9 wt.% CaO equivalent, while preserving important inter-instrument differences in several components.

After 15 min contact with 2.00 g clay in 40.0 mL solution, Ca^{2+} showed apparent reductions of 6.67%, 4.11%, and 3.45% at the Low, Actual, and High levels. Mg^{2+} showed corresponding apparent reductions of 36.00%, 12.24%, and 8.81%. These results demonstrate measurable changes in dissolved divalent-cation concentrations under the tested conditions, with a larger descriptive relative decrease for Mg^{2+}. Because the clay-contact tests were unreplicated and no mineralogical or post-contact speciation

measurements were available, the observed changes cannot be assigned to adsorption, ion exchange, precipitation, or any single mechanism. The study therefore provides a field-referenced baseline for Ca^{2+}/Mg^{2+}–clay interaction in the Derna system and identifies the measurements required for future mechanistic and process-level evaluation.

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