



Compositional and structural controls on Fe(III) trapping in LDH phases

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ARTICLE INFO

Keywords:

Layered double hydroxides
Iron incorporation
Pair distribution function
X-ray absorption spectroscopy
Density functional theory

ABSTRACT

Understanding Fe incorporation in layered double hydroxide (LDH) phases is important for revealing the steel/cement interface interaction in low carbon cement. In this study, synchrotron-based characterization is combined with density functional theory (DFT) calculations to unravel the atomistic mechanisms controlling Fe(III) incorporation in Mg–Al LDHs as a function of composition and local structure. XAS measurements reveal that Fe incorporation is strongly suppressed under trivalent-cation-rich compositions, leading to a preferential association of Fe with edge or defect-related environments. The spectra indicate that Fe(III) is incorporated into the LDH lattice in a well-defined octahedral environment under Mg-rich compositions. DFT calculations of substitution energies support these findings by showing that Fe(III) substitution for Al(III) in the main layers is strongly composition-dependent: Fe(III) incorporation is most unfavorable at Al-rich compositions but becomes progressively more favorable in Mg-rich environments. In Al-rich LDHs, Fe shortens neighboring Al–O bonds, introducing local strain and lowering mechanical stability, while in Mg-rich LDHs the more flexible Mg–O framework accommodates Fe(III) more effectively. Overall, this study defines molecular-level constraints governing Fe(III) incorporation into LDH phases in low-carbon cements. The results offer transferable insights concerning the influence of LDH composition on the interfacial phase assemblages relevant to steel corrosion protection.

1. Introduction

The production of conventional Portland cement is associated with substantial carbon dioxide emissions [1,2]: those emissions can efficiently be lowered through partial replacement of the Portland cement by supplementary cementitious materials (SCMs) such as metallurgical slags and combustion ashes, which may have a relatively high content of SiO₂, MgO, and/or Al₂O₃ [3]. The use of Mg- and Al-rich SCMs such as slags in Portland cement can promote the formation of Mg–Al layered double hydroxides (LDHs) in hydration products under conditions of high pH and sufficient Mg and Al availability [4–6]. In alkali-activated slag cement systems, the nature of the activator controls the type of LDH formed: hydroxide activation generally leads to the formation of

OH[−] intercalated LDHs, whereas carbonate activation (e.g., Na₂CO₃) promotes the formation of CO₃^{2−} intercalated LDHs [7,8]. Recently, magnesia-based cements, particularly magnesium carbonate cements, are being developed to minimize chemical CO₂ emissions. Magnesium carbonate cements are characterized by their high MgO content, which favors the formation of LDHs when blended with Al-rich SCMs [9,10]. The development of low-carbon cements can be associated with the formation of Mg–Al LDH phases in the hydration products under alkali and Mg, Al rich conditions.

The general chemical formula of LDH can be expressed as M(II)_{1−x}M(III)_x(OH)₂(A_{x/n}^{n−})_y·y(H₂O), where divalent cations (M(II)) such as Mg(II) and trivalent cations (M(III)) such as Al(III) form the positively charged main layers [11,12] together with OH[−] groups. These layers are balanced

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by interlayer anions (A^{n-}) including carbonate, sulfate, chloride, and hydroxide, along with water molecules. The incorporation of additional metal cations with similar ionic radii and valence states to Mg(II) and Al (III), provided for example from a cement pore solution, results in the formation of multicomponent solid solutions in the main layer [5,13–15]. Specifically, octahedrally coordinated Fe(II) (0.78 Å) and Fe(III) (0.65 Å) species present in cement, or SCMs, or originating from steel corrosion, possess ionic radii that are relatively similar to those of Mg(II) (0.72 Å) and Al(III) (0.54 Å) [16]. This similarity in ionic radii allows for isomorphic substitution within the LDH main layers, thereby enabling the formation of Mg(II)/Fe(II)-Al(III)/Fe(III) LDH solid solutions. Recently some researchers have demonstrated that Mg-Al/Fe LDHs can be formed in situ around steel reinforcement in alkaline environments with available magnesium sources, where Al(III) is partially replaced by Fe(III) released from the steel substrate as the Fe donor [17,18]. In addition, some investigations have also shown that in low carbon cements, passive films on reinforcing steel contained not only iron oxides but also LDH-like phases [19]. This type of passive film is more porous than the iron oxides formed in traditional Portland cement concretes, providing a weaker protection for steel and thus resulting in increased susceptibility to steel corrosion [19].

Steel is an essential structural material extensively employed throughout the construction sector. The economic impact associated with corrosion of steel, particularly in reinforced concretes, represents a substantial global financial burden [20]. Recently, the anion-exchange capability of LDH phases has been investigated for their potential to immobilize chloride and sulfate ions, thereby removing them from concrete pore fluids and mitigating their potential to accelerate steel corrosion [21]. However, the mechanisms of cation exchange/incorporation in LDH phases, particularly for Fe, remain insufficiently understood. Such incorporation may influence the properties of the steel-hydrated cement interface, including the stability and protective performance of passivation layers [19]. This issue becomes more critical in blended and magnesia-based cements, where the pore solution pH is lower than in Portland cement and LDH phases are commonly present [22–25].

In Portland cement, where little MgO is present, iron from steel can form a dense, protective iron oxide passivation layer - typically composed of goethite (α -FeOOH), lepidocrocite (γ -FeOOH), and hematite (α -Fe₂O₃) - that effectively shields the steel surface from further oxygen and moisture ingress [26,27]. The density of Fe-doped LDH phases (2.03–2.33 g/cm³ [13]) is much smaller than those of goethite (ρ = 4.26 g/cm³), lepidocrocite (ρ = 4.00 g/cm³), and hematite (ρ = 5.25 g/cm³) [28,29] formed in the passivation film. This contrast suggests that the partitioning of Fe between LDH phases and iron oxides influences the compactness and protective performance of the resulting passivation layer [19]. This difference in compactness implies a higher degree of porosity, which leads to increased permeability relative to the dense Fe-oxide passivation films typically observed in Portland cement concretes [19]. Thus, understanding the interaction between LDHs and Fe species is essential in clarifying the competitive mechanisms that govern Fe partitioning at the steel-cement interface. Limiting Fe incorporation into LDHs and increasing the fraction of Fe present as iron oxides are key to enhance the performance of passivation layers. Such insights are particularly relevant for steel protection in low-carbon cement concretes, where LDHs are widely present. In addition, they provide a basis for developing reliable thermodynamic databases to predict LDH phase stability and composition.

In this study, Fe(III)-bearing Mg—Al LDHs with systematically varied compositions were investigated. Experimental and computational methods were used to investigate the limits of Fe(III) substitution. Synchrotron-based X-ray absorption spectroscopy (XAS) was used to characterize the local coordination environments of Fe(III), while molecular simulations computed the relative formation energies of Fe-LDH phases and local strains. Understanding the substitution behavior of Fe (III) in LDH provides a theoretical basis for understanding the factors

controlling the distribution of iron between LDH structures and iron (hydr)oxides protecting steel from further corrosion and thus a step toward the development of cementitious materials with enhanced corrosion protection for steel reinforcement.

2. Materials and methods

2.1. Materials

All chemical reagents employed in this study, including magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O), ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O), sodium hydroxide (NaOH), and sodium carbonate (Na₂CO₃), were of analytical grade (Sigma-Aldrich) and used as received without additional purification. All solutions were prepared using ultrapure water (resistivity = 18.2 MΩ·cm) obtained from a Millipore Synergy water purification system.

2.2. Fe(III) introduction in Mg—Al LDH with different M(II)/M(III)

Mg—Al LDHs with different M(II)/M(III) ratios were prepared using the coprecipitation method to simulate LDH formation in cementitious environment [30]. The coprecipitation method is employed as a simplified model to simulate LDH formation in cementitious environments, where LDHs form through dissolution-precipitation processes under alkaline conditions. By controlling solution chemistry and cation ratios, this approach captures the key mechanisms governing LDH formation through precipitation process, although it does not fully reproduce the complexity of real cement systems. The precursor solutions were prepared using a mixture of metal nitrates, with the Mg/(Al + Fe) molar ratios adjusted to 2.0, 3.0, 4.0, and 5.0, while maintaining a constant Fe/(Mg + Al) molar ratio of 0.125. The Fe/(Mg + Al) molar ratio was fixed at 0.125 to represent a moderate level of Fe incorporation while maintaining LDH structural stability. This value is also supported by DFT calculations in section 2.4, which suggest an upper substitution limit of ~16.6% Fe in a 5:1 cation configuration. For the 3:1 LDH structure, this corresponds to an approximately 1:1 substitution between Al and Fe at the trivalent cation sites. This composition corresponds to the theoretical stoichiometry of Mg₄₋₁₀Al_xFe_{2-x}(OH)₁₂₋₂₄CO₃·nH₂O, where x = 1.25, 1, 0.75, and 0.5, respectively. An alkaline precipitating agent was prepared using 1.3 M NaOH and Na₂CO₃, with the carbonate concentration maintained at double the stoichiometric requirement for carbonate-LDH to guarantee complete anion intercalation. The synthesis process was carried out under controlled conditions, maintaining the pH at around 12 throughout. Detailed information on the reagents used is provided in Table 1.

The addition procedure was carried out using a precisely controlled dual-solution addition method, as detailed in previous research [14]. The resulting colloidal suspension was then subjected to hydrothermal treatment in a temperature-controlled convection oven (ED 23, Binder GmbH, Germany) maintained at 65 ± 0.5 °C for 48 h. After the aging process, the precipitate was collected and subjected to an extensive washing protocol with ultrapure water (Milli-Q, 18.2 MΩ·cm) until the supernatant conductivity reached <100 μS/cm, indicating effective removal of ionic byproducts. To guarantee complete carbonate

Table 1
The chemicals used during Fe introduction in Mg—Al LDHs.

Sample name	Nitrate metal solution			Alkali solution	
	Mg (NO ₃) ₂ ·6H ₂ O	Al (NO ₃) ₃ ·9H ₂ O	Fe (NO ₃) ₃ ·9H ₂ O	NaOH	Na ₂ CO ₃
2:1	0.40 M	0.125 M	0.075 M	1.3 M	0.20 M
3:1	0.45 M	0.075 M	0.075 M	1.3 M	0.15 M
4:1	0.48 M	0.045 M	0.075 M	1.3 M	0.12 M
5:1	0.50 M	0.025 M	0.075 M	1.3 M	0.10 M

intercalation and enhance crystallinity, the washed product was redispersed in 500 mL of 0.3 M sodium carbonate solution and subjected to secondary hydrothermal aging at 65 °C for 24 h. The final product was then washed to ultrahigh purity (conductivity <50 $\mu\text{S}/\text{cm}$) and dried in an oven at 60 °C for 48 h. The dried material was mechanically ground using an agate mortar and pestle for ~ 10 min until a fine and homogeneous powder was obtained. Grinding was performed under ambient conditions. After grinding, the sample was sieved through a 63 μm mesh to obtain uniformly sized particles for further characterization.

To determine the elemental ratio in the dried LDH solids, ~ 20 mg of Mg-Al/Fe LDH was dissolved in 15 mL of 5% HNO_3 and subsequently diluted tenfold. The solutions were analyzed by ICP-OES (Agilent 5110 VDV, USA), with Mg (285.213 nm), Al (394.401 nm), and Fe (234.350 nm) quantified against six-point calibration curves (0.1–50 ppm). Each measurement was performed in triplicate; mean values are reported in Table 2.

2.3. Solid phase characterization

2.3.1. Phase assemblage

2.3.1.1. Powder X-ray diffraction (PXRD). PXRD was employed to investigate the structure of the Mg-Al/Fe LDHs with different M(II)/M(III) obtained under coprecipitation and clarify whether there was a Fe phase separation during Fe introduction to LDH. The powder was gently packed into a standard sample holder to minimize preferred orientation effects, and the surface was carefully leveled using a glass slide to ensure a smooth, flat profile for measurement. Diffraction data were collected using a Rigaku SmartLab SE X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$), operating in θ - θ geometry, in which the X-ray source and detector move symmetrically while the sample remains stationary. Scans were performed over a 2θ range of 5° – 75° with a step size of 0.01° and a scan rate of $2.5^\circ/\text{min}$. To verify instrument stability and data reliability, calibration checks were performed using a CaF_2 standard (AR grade, 99.5% purity, Aladdin) at the beginning and end of each measurement session. The characteristic (003) (related to the interlayer spacing) and (110) (related to the main layer cation distance) reflections of the LDH phase were analyzed using the Bragg equation [31]. The d-spacings (003 and 110) were calculated from the peak positions to assess structural changes induced by M(II)/M(III).

2.3.1.2. Pair distribution function (PDF) analysis. Considering that the cation-cation distance derived from PXRD represents an averaged value over long-range ordered symmetry units, it only captures the broader structural features of LDH. Therefore, to obtain a comprehensive picture, we further employed PDF analysis based on high-energy X-ray scattering (HEXS) data. This can be used to extract real-space distance distributions between all atomic pairs, revealing both short-range (local

and medium-range ordering. The HEXS experiments were conducted at the ID11 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. An X-ray beam with an energy of 90.65 keV ($\lambda = 0.1368 \text{ \AA}$) was employed for the measurements. The beam spot size was set at $300 \times 300 \mu\text{m}$. Before the measurement, powdered LDHs were packed into $\varnothing 1$ mm polyimide capillaries (Cole-Parmer, United States) and sealed with epoxy glue. The X-ray energy was calibrated by measuring diffraction peaks of a single-crystal silicon cube ($100 \mu\text{m}$) and the instrument geometry was obtained from a CeO_2 powder diffraction measurement. An empty capillary was used for background subtraction. Data processing, including the extraction of structure factors and PDFs, was performed using the xPDFsuite code [32].

2.3.1.3. Raman spectroscopy. Raman spectroscopy was employed to identify Fe phases among LDHs after same amount of Fe introduction and semi-quantitatively assess the M(II)/M(III) ratio in the main layer of Mg-Al/Fe LDHs. Sieved samples ($< 63 \mu\text{m}$) were uniformly dispersed on a glass slide and lightly pressed to ensure a flat, homogeneous surface, optimizing laser focus and signal reproducibility. Measurements were performed using a portable BWS415-785S Raman spectrometer (B&WTEK Ltd., USA) with a 785 nm diode laser excitation source. A long-working-distance $20\times$ objective lens (L PLAN 20/0.40, NA = 0.40, WD = 12 mm) was used to collect scattered light while minimizing sample disturbance. Spectra were acquired across 158 – 3240 cm^{-1} with an integration time of 60 s and two accumulations per scan to enhance the signal-to-noise ratio. Post-acquisition, baseline correction was applied using BWSpec software to remove fluorescence background and instrumental artifacts. The resulting spectra were analyzed to correlate vibrational modes with cation occupancy, particularly focusing on bands sensitive to the local coordination environment of Mg, Al, and Fe within the LDH layers.

2.3.1.4. Ultraviolet-visible spectroscopy (UV-Vis). UV-VIS measurements were conducted using a Varian Cary 4000 UV-Vis spectrophotometer to identify iron phases among LDHs after same amount of Fe incorporation. Approximately 0.3 g of the sample was packed for measurement. A barium sulfate background was used prior to sample analysis to correct baseline interference. The spectra were recorded in Kubelka-Munk function ($F(R)$) [33] mode, spanning a wavelength range of 200–800 nm. An automatic beam source switch occurred at 350 nm, with a scanning rate of 600 nm/min and a data interval of 1 nm. Normalization of the absorption data in the 200–600 nm range was performed for the iron oxide phases determination.

2.3.2. X-ray absorption spectroscopy (XAS)

Fe K-edge X-ray absorption spectroscopy (XAS) measurements were performed at the SAMBA beamline of the SOLEIL synchrotron facility, the P65 beamline of the DESY synchrotron facility, and the BL22 CLÆSS Beamline at ALBA, to investigate the local coordination environment of Fe in Mg–Al LDHs with different M(II)/M(III) ratios after same amount of Fe introduction. The XAS measurements were conducted at three different beamlines to accommodate the large number and complexity of the Fe-containing samples considering the limited time available for allocation at each individual facility. The experiments utilized a Si(111) double-crystal monochromator with an energy resolution of approximately 0.5 eV at 7.1 keV, with data collected in transmission mode using Oxford ionization chambers. Energy calibration was continuously monitored using an Fe foil reference, with its first absorption edge set to 7112 eV. All samples, including the LDHs and reference compounds (goethite, hematite, and 2-line ferrihydrite), were uniformly mixed with graphite to minimize self-absorption effects and pressed into pellets. Prior to measurements, the LDH pellets were encapsulated with Kapton tape on both surfaces to prevent dehydration and ensure measurement stability. To reduce thermal disorder effects, samples were maintained at approximately 77 K during data collection using a liquid nitrogen

Table 2
Measured elemental mol% and molar ratios in Mg-Al/Fe LDHs.

Sample ^a	Mg (mol %)	Al (mol%)	Fe (mol%)	Mg/(Al + Fe) ^c	Fe/(Mg + Al + Fe) ^c
2:1 ^b	69.0 $\pm$ 0.4	18.7 $\pm$ 0.3	12.3 $\pm$ 0.1	2.2 $\pm$ 0.1 (2)	0.123 $\pm$ 0.001 (0.125)
3:1	76.4 $\pm$ 0.1	11.3 $\pm$ 0.1	12.3 $\pm$ 0.1	3.2 $\pm$ 0.1 (3)	0.123 $\pm$ 0.001 (0.125)
4:1	80.9 $\pm$ 0.1	6.8 $\pm$ 0.1	12.3 $\pm$ 0.1	4.2 $\pm$ 0.1	0.123 $\pm$ 0.001
5:1	83.9 $\pm$ 0.1	3.9 $\pm$ 0.1	12.2 $\pm$ 0.1	5.2 $\pm$ 0.1 (5)	0.122 $\pm$ 0.001 (0.125)

^a Total Mg:Al:Fe = 4:1.09:0.71, 6:0.89:0.96, 8:0.68:1.21, and 10:0.46:1.46.

^b Considering the formation of ferrihydrite (shown in section 3.2), the effective Mg:Al:Fe in the 2:1 sample corresponds to 4:1.09:0.48 (Mg/(Al + Fe) = 2.6 and Al/Fe = 1.5).

^c The numbers in parentheses represent the ratios used in the DFT simulation.

cryostat.

The acquired X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were processed and analyzed using the Demeter software package [34]. Athena was employed for XANES spectral processing, including energy alignment, background subtraction, and normalization. Linear combination fitting (LCF) of the Fe K-edge XANES spectra was performed to quantitatively determine the relative proportions of different Fe species present in the samples. For EXAFS analysis, the k^3 -weighted spectra were Fourier transformed over a k -range of 2.0–12.0 Å⁻¹ using a Hanning window function to minimize truncation effects. The amplitude reduction factor was determined by fitting the reference goethite spectrum. Theoretical scattering paths for Fe coordination environments were generated using FEFF6 calculations, with ferrihydrite and pyroaurite serving as model structures.

To further resolve the second-shell coordination environment of Fe in the LDH layers, wavelet transform (WT) analysis was conducted using the HAMA FORTRAN code (obtained from BM20 at ESRF) [35,36]. The WT calculations employed the Morlet wavelet method with optimized parameters ($\kappa \approx 2D$ and $\sigma = 1$), where κ represents the wavelet oscillation frequency and D is the interatomic distance.

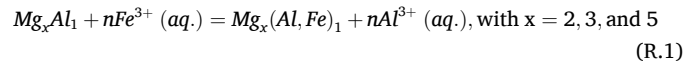
2.3.3. Thermogravimetry (TGA)

The relative compositions of the LDH samples were determined using thermogravimetric analysis (TGA). Measurements were performed on a Netzsch STA 449 F3 Jupiter thermal analyzer (Germany). Approximately 40 mg of sample powder was loaded into an alumina crucible and subjected to heating from 30 to 1000 °C at a constant rate of 10 °C/min under a continuous nitrogen purge (20 mL/min) [5].

2.4. Ab initio structure modeling

The LDH with different M(II)/M(III) ratios were modelled using $2 \times 2 \times 2$ supercells, containing 96 metal cations. For the sake of computational efficiency, the original trigonal cell was transformed into an equivalent orthorhombic cell with dimensions of 21.56 Å, 15.33 Å, and 18.73 Å in x , y , and z directions, respectively.

First-principles calculations were performed with CP2K (Quickstep, GPW) [37] using the PBE exchange-correlation functional [38] with D3-dispersion correction [39], dual-space GTH-pseudopotentials [40], and DZVP-MOLOPT-SR-GTH basis sets [41]. Plane-wave cutoffs of 800 Ry with a REL_CUTOFF 80 Ry. The wavefunction was optimized better than 1×10^{-7} Hartree and the energy was calculated for Γ -point only. Spin-polarized calculations with Fe in a high-spin Fe(III) state were used. A Hubbard potential $U(1.9 \text{ eV})$ were applied to 3d electrons of Fe to improve the known poor performance of DFT for highly localized states. Structures were relaxed until interatomic forces reached 4.5×10^{-4} Hartree/Bohr. Interlayer compositions including CO_3^{2-} and H_2O were chosen based on charge balance and TGA-derived water contents on a per-formula-unit basis, corresponding to the specific M(II)/M(III) ratios. The numbers of carbonate and water molecules used in the structural models were then scaled proportionally to the supercell size, resulting in 8 CO_3^{2-} and 32 H_2O , 6 CO_3^{2-} and 30 H_2O , and 4 CO_3^{2-} and 23 H_2O for the different M(II)/M(III) ratios (2, 3, 5) considered. The interlayer species were placed randomly and relaxed via ab initio molecular dynamics for 3 ps with a time step of 0.5 fs at 300 K in NVT ensemble with CSV thermostat [42], followed by geometry optimization. For each composition, symmetry-inequivalent Fe distributions were enumerated and optimized, based on the principle that the trivalent cations are located as far away as possible from each other. The model selection is based on energy evaluation of various configurations, where the configuration with lowest energy was used for Fe incorporation. The Gibbs free energy of Fe incorporation was calculated based on reaction 1 (R.1) and the Gibbs free energy was calculated by Eq. 1.



$$\Delta G = \Delta E(\text{el.}) + \Delta G_{\text{vib}}(T) + p\Delta V \quad (1)$$

where $\Delta E(\text{el.})$ is the potential energy difference obtained directly from reaction R.1, $\Delta G_{\text{vib}}(T)$ is vibrational energy and $p\Delta V$ is the volume contribution. The $p\Delta V$ contribution is typically negligible in solid-state systems; although Fe incorporation leads to a slight increase in cell volume, the resulting change is minimal and can therefore be safely neglected. Hence, the free energy is formulated to Eq.2.

$$\Delta G \approx \Delta F = \Delta E(\text{el.}) + \Delta G_{\text{vib}}(T) \quad (2)$$

The free energy is calculated via vibrational analysis with thermal correction as showed in Eq.3.

$$\Delta G_{\text{vib}}(T) \cong \Delta ZPE + \Delta U_{\text{vib}}(T) - T\Delta S \quad (3)$$

With:

$$ZPE = \sum_i \frac{h\nu_i}{2} \quad (4)$$

$$U_{\text{vib}}(T) = \sum_i \frac{h\nu_i}{e^{\left(\frac{h\nu_i}{k_B T}\right)} - 1} \quad (5)$$

$$S = k_B \sum \left[\frac{\frac{\theta_{v,K}}{T}}{e^{\frac{\theta_{v,K}}{T}} - 1} - \ln \left(1 - e^{-\frac{\theta_{v,K}}{T}} \right) \right] \quad (6)$$

$$\text{with } \theta_{v,K} = \frac{h\nu_i}{k_B} \quad (7)$$

ΔZPE is the zero-point energy (ZPE) difference, $\Delta U_{\text{vib}}(T)$ is the thermal vibrational energy correction, T is the temperature, and the ΔS is the difference of vibrational entropy. All thermodynamic quantities were evaluated at 298.15 K. The corresponding thermal vibrational energy corrections and vibrational entropies were obtained from vibrational calculation, and converted to energy through Eq. 4, Eq. 5, Eq. 6, and Eq. 7, respectively, where h is the Planck constant, k_B is the Boltzmann constant, ν_i is the vibrational frequency of vibrational mode i , and T is the temperature. Bulk modulus calculation is also based on the DFT calculation by variation of the lattice parameter of different M(II)/M(III) ratios of LDH structures, where the bulk modulus is determined by fitting the curve to Birch-Murnaghan equation of state. For directional stress calculations, a stress tensor is imposed, and the structure is optimized while the cell remains fixed. Details of the deformation calculations are discussed in the Supporting Information. For XAS spectral simulation, FEFF7 was used to simulate EXAFS of Fe from DFT-optimized structures in comparison to experiment, and the component ratio is determined by a linear combination of two species. For spectral simulation with the FEFF code, corrections of 3.0 eV and 1.0 eV for real shift and imaginary shift (respectively) were given to correct the error in Fermi energy estimation. The amplitude reduction (S_0^2) was set to 0.8 and the broadening factor was set to 0.9 eV (HOLE 1 0.9).

3. Results and discussion

3.1. Phase assemblage

The powder X-ray diffraction (PXRD) patterns of LDHs with M(II)/M(III) ratios ranging from 2:1 to 5:1 are shown in Fig. 1a; note that all samples contain 12.5 mol% of Fe(III). They exhibit the characteristic peaks corresponding to a LDH structure [30], with diffraction peaks observed at approximately 11° (003), 22° (006), 34° (012), 38° (015), 45° (018), 60° (110), 61° (113), and 65° (116) 2 θ . As the M(II)/M(III)

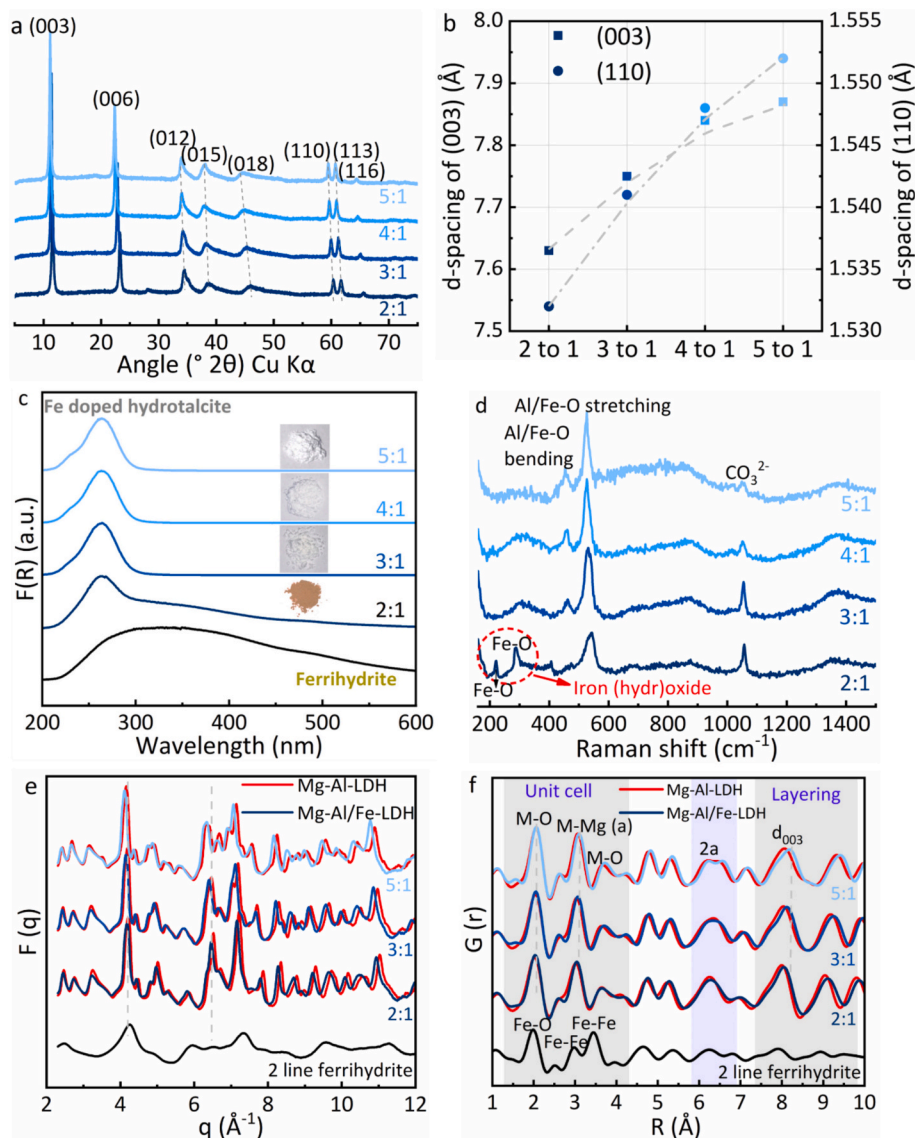


Fig. 1. Structural characterization of Mg-Al/Fe layered double hydroxides with M(II)/M(III) ratios from 2:1 to 5:1 with 12.5 mol% of Fe(III) of all cations. (a) PXRD patterns, (b) d-spacing of (003) and (110), (c) UV-Vis absorption spectra, (d) Raman spectra; Pair distribution function analysis of synchrotron-based X-ray scattering data for 2-line ferrihydrite as an additional reference: (e) Reduced structure factor, $F(q) = q(S(q) - 1)$ and (f) Background subtracted pair distribution functions.

ratio increases, all diffraction peaks shift to lower angles. The shift depends on the specific crystallographic plane. The (003) plane reflection is associated with the interlayer spacing, while the (110) plane reflection corresponds to the main layer metal-metal distance [43]. Based on the Bragg equation [31], these shifts are quantitatively analyzed to calculate changes in the interlayer spacing and the metal-metal distances with M(II)/M(III) ratios increasing in the Fe doped LDH structure (Fig. 1b). As the ratio of M(II)/M(III) increases from 2:1 to 5:1, the interlayer spacing ((003) plane) expands from 7.63 Å to 7.87 Å, while the mean metal-metal distance, which is double the (110) spacing, increases from 3.064 to 3.114 Å. The larger interlayer spacing can be attributed to the weaker electrostatic interaction between interlayer anions and the main layer due to the lower charge density of the structures with the low M(II) cations loading, while the larger metal-metal distance results from the longer average M(II)-O bond lengths compared to M(III)-O [44].

Iron (hydr)oxide peaks are absent from the PXRD patterns, likely due to the amorphous nature of these additional Fe-containing phases in the samples, although distinct differences in color are evident between the samples indicating the possible formation of iron (hydr)oxides. UV-Vis spectroscopy (Fig. 1c) is used to qualitatively assess the potential

formation of iron (hydr)oxides; in LDH structures, the absorptions are concentrated in the range of 250–300 nm resulting from charge transfer transitions between metal and OH groups, [45] while iron (hydr)oxides exhibit broad features primarily in the 300–400 nm and ~ 500 nm regions, attributed to d-d electronic excitations in Fe(III) [14,46]. As shown in Fig. 1c, the broad visible-region absorption feature observed in the 2:1 sample shows good agreement with the reference, supporting its assignment to amorphous iron (hydr)oxide. This observation suggests that in the 2:1 sample, only a fraction of the Fe atoms is incorporated into the LDH lattice, and the rest are present as a separate iron (hydr)oxide phase.

Raman spectroscopy (Fig. 1d) provides semi-quantitative evidence that aligns with the UV-Vis results. The 2:1 sample exhibits distinct Fe—O vibrational peaks at approximately 219 and 287 cm^{-1} [47], indicating the presence of iron (hydr)oxide solids, while these peaks are absent in the other samples. All samples show the characteristic Al/Fe-O bending and stretching modes from the LDH phase at around 459 and 530 cm^{-1} , as well as C—O vibrations near 1050 cm^{-1} from the interlayer CO_3^{2-} [48,49]. The Al/Fe-O bending and stretching vibration peaks are clearly observed in samples with M(II)/M(III) ratios between 3 and 5,

while their intensity is significantly weaker in the 2:1 sample. The presence of iron (hydr)oxide solids indicates that in the 2:1 sample, less Fe is incorporated into the LDH main layer, indicating a lower degree of structural integration of Fe within the LDH phase with M(II)/M(III) at 2. The weakening of C—O vibrations with increasing M(II)/M(III) ratio may be associated with a decrease in interlayer CO_3^{2-} , consistent with the reduced positive layer charge [14,50].

Pair distribution function (PDF) analysis can offer more detailed insights into the local and intermediate-range atomic arrangements of mineral structures, beyond the averaged information obtained from conventional XRD [51]. Even subtle differences in interatomic distances can become amplified through periodic atomic correlations at longer length scales. As shown in Fig. 1e, the reduced structure factor, $F(q)$, profiles of the LDH samples exhibit noticeable shifts in oscillation features. Upon substituting Al(III) with Fe(III) at constant M(II)/M(III) ratios, the $F(q)$ peaks systematically shift to lower q values, indicating an increase in average real-space interatomic distances. Similarly, increasing the M(II)/M(III) ratio from 2:1 to 5:1 also results in a leftward shift of $F(q)$ oscillations, further supporting the identification of expansion of the lattice due to higher M(II) content and larger ionic radii. The comparison with the ferrihydrite reference shows even for the 2:1 sample only a minor contribution of ferrihydrite to the observed signal, due to the relatively more random bond length distribution compared to LDH structure with higher crystallinity.

Fig. 1f presents the corresponding $G(r)$ functions, representing the probability of finding pairs of atoms separated by a distance r , obtained from the Fourier transform of the total scattering data [51]. Below 4 Å, the peaks primarily reflect intralayer unit cell features, such as the metal-oxygen (Me—O) bond in the octahedral layer [52]. The Me—O

distance increases from 2.03 Å in the 2:1 sample to 2.06 Å in the 5:1 sample as the contribution of Mg—O bonds (which are longer than Al—O and Fe—O bonds) becomes more dominant. Concurrently, the nearest Me—Mg distance, corresponding to a lattice parameter, increases from 3.05 Å to 3.10 Å, consistent with the XRD-derived (110) reflection trend illustrated in Fig. 1a. At around 6 Å, which corresponds to approximately double the a lattice parameter [53], differences in medium-range order are evident. In the 2:1 sample, there is only one type of Mg—Al/Fe edge-edge sharing configuration, and no Mg—Mg edge-edge configurations (section 3.4). Moreover, the identical position of the ~6 Å peak in Fe-free and Fe-bearing 2:1 LDH samples indicates that Fe incorporation does not significantly alter the average interatomic spacing at this low Mg to M(III) ratio. In contrast, in the 3:1 and 5:1 samples, both Fe-free and Fe-containing LDHs exhibit peak splitting around 6 Å, indicating two distinct interatomic distances. The longer one corresponds to Mg—(O—Mg—O)—Mg and the shorter one represents Al/Fe—(O—Mg—O)—Al/Fe. This indicates the different distance of Me—(OH)₂—Me edge-edge sharing in 3:1 and 5:1 sample. This observation is supported by results of atomistic simulations described in section 3.4. The greater variation in Mg—(OH)₂—Mg distances observed in the 3:1 and 5:1 samples compared to the 2:1 sample indicates reduced structural rigidity in the former, which is related to the lower stiffness of Me(II)—O bond as discussed further in section 3.4. Notably, the Fe-containing samples show a shift to larger in-layer lattice parameters compared to their Fe-free counterparts, implying that Fe incorporation introduces a larger structure expansion and needs a ‘softer’ structure to accommodate the Fe substitutions.

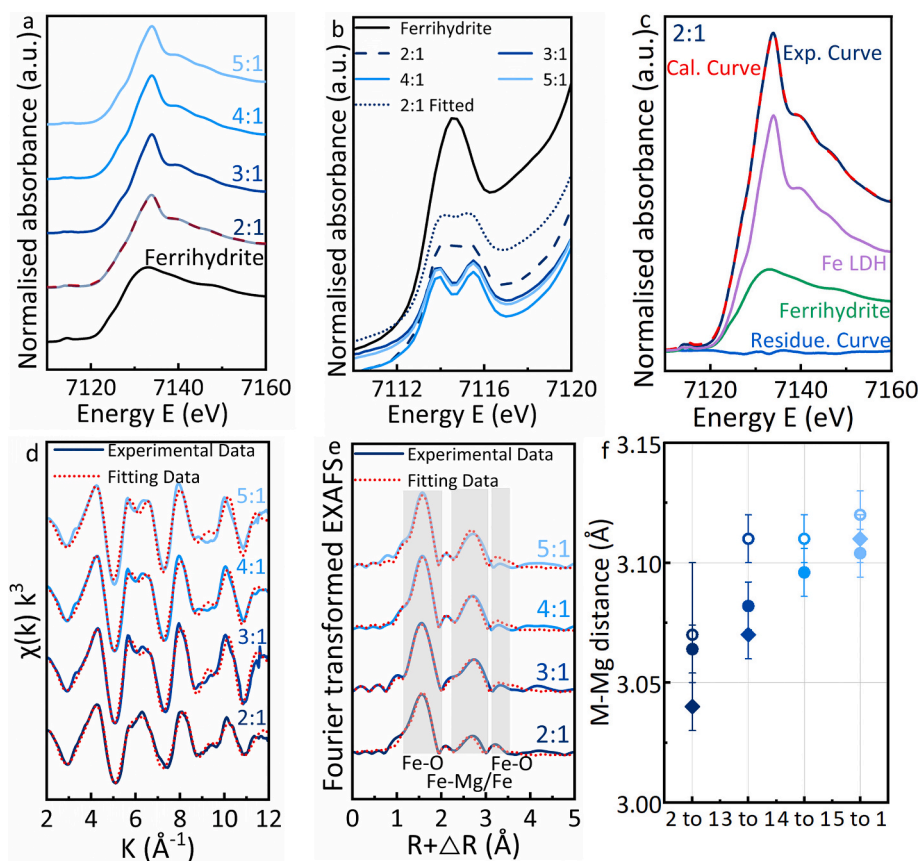


Fig. 2. X-ray adsorption spectroscopy analysis for LDHs with M(II)/M(III) ratios from 2:1 to 5:1 with and without 12.5 mol% Fe incorporation. (a) Normalized Fe K-edge XANES spectra, (b) enlarged pre-edge features from Fe K-edge XANES spectra, (c) Linear combination fitting for Fe K-edge XANES spectrum of 2:1 sample, (d) Comparison of k^3 -weighted Fe K-edge EXAFS spectra and shell best fit, (e) Corresponding Fourier transforms in R space and the best fit, (f) Comparison of metal-Mg distances obtained from PXRD (full circles), EXAFS fitting (empty circles), and PDF fitting (full diamonds).

3.2. Fe coordination environment

The analysis of XANES spectra in the 7110–7160 eV range (Fig. 2a) reveals variations in the local electronic structure of Fe among samples with different M(II)/M(III) ratios [54]. The pre-edge and main edge features in the Fe K-edge XANES spectra observed at approximately 7115 and 7132 eV are attributed to electronic transitions in Fe from the 1 s core level to unoccupied 3d and 4p orbitals, respectively [55,56]. All spectra of samples with M(II)/M(III) ratios $\geq 3:1$ exhibit a characteristic shoulder near E_0 (~ 7126 eV), which is less evident in the 2:1 sample and absent from the reference ferrihydrite. Notably, the white line (around 7134 eV) is sharp in samples with M(II)/M(III) ratios $\geq 3:1$ but broadens in the 2:1 sample. This indicates clearly different local structural environments of Fe (lower coordination number due to the presence of ferrihydrite [57]) in LDH samples with M(II)/M(III) = 2. Further details of the pre-edge feature are enlarged in Fig. 2b. The single absorption peak at ~ 7114.5 eV with higher intensity observed for pure ferrihydrite, compared to Fe in LDHs, suggests that Fe atoms are situated in a non-centrosymmetric coordination environment characteristic of high-spin Fe(III) in a disordered or amorphous structure [55].

The spectral profile evolves from a near singlet to a split doublet pattern (characteristic for LDH) when moving from 2:1 to 5:1, indicating an increase in the symmetry of Fe coordination environments with increasing M(II)/M(III) ratio. These observations suggest that the local Fe environment is strongly influenced by the M(II)/M(III) ratio in the main layer.

The k^3 -weighted Fe K-edge EXAFS spectra of the LDH with varying M(II)/M(III) ratios and the same Fe/Al ratio are shown in Fig. 2d, which exhibit distinct oscillation patterns in the χ range from $2 \text{ \AA}^{-1}$ to $12 \text{ \AA}^{-1}$. A characteristic beat pattern near $6 \text{ \AA}^{-1}$ in all samples except for the 2:1 sample results from the interference between two different sinusoidal components at approximately 5.6 and $6.4 \text{ \AA}^{-1}$, which is a typical characteristic of LDH phases [58]. In the 2:1 sample, the oscillation at $\sim 5.6 \text{ \AA}^{-1}$ is significantly attenuated. Additionally, while the other samples show a single sinusoidal component in the oscillation near $10.1 \text{ \AA}^{-1}$, the 2:1 sample exhibits pronounced sinusoidal contributions not only at

$10.1 \text{ \AA}^{-1}$ but also at $\sim 10.5 \text{ \AA}^{-1}$, indicating the presence of a secondary phase. After Fourier transformation (Fig. 2e), the first and third coordination shells are unambiguously attributed to Fe–O backscattering pair. However, the second shell is more difficult to assign. Based on Fe K-edge XANES fitting results for the 2:1 sample (Fig. 2c), the second shell represents a combination of Fe–Fe scattering from ferrihydrite (20 wt %) and Fe–Mg scattering from the LDH phase (80 wt %).

To clarify whether there is a mixed backscattering path for the second shell, the wavelet transform (Fig. 3) is conducted using optimized Morlet parameters ($\kappa = 10$ and $\sigma = 1$) and a k^3 -weighted signal. The first coordination shell, corresponding to Fe–O backscattering pair, appears at $R + \Delta R \approx 1.5 \text{ \AA}$ and $k \approx 6.5 \text{ \AA}^{-1}$ across all samples with M(II)/M(III) ratios from 2:1 to 5:1. In the 2:1 sample, the second shell (at $R + \Delta R \approx 2.6 \text{ \AA}$) exhibits one broad maximum from $k \approx 5 \text{ \AA}^{-1}$ to $k \approx 9 \text{ \AA}^{-1}$, suggesting a combination of Fe–Mg and Fe–Fe backscattering paths, originating from the LDH phase and ferrihydrite, respectively. In addition, lower first and second shell intensities in 2:1 sample than other ratios indicate a lower coordination number. In contrast, the other samples show only a single maximum centered around $k \approx 6.5 \text{ \AA}^{-1}$ in the second shell, indicating a more uniform Fe–Mg coordination environment. Therefore, the EXAFS signal in this region of 2:1 sample can be interpreted as a combination of these two backscattering contributions.

Detailed information about Fe coordination in LDH with varying M(II)/M(III) ratios is reported in Table S1, obtained from the quantitative EXAFS fitting results. Based on observations from the Wavelet analysis, two backscattering paths are chosen for the second shell of the 2:1 sample. The backscattering path at lower k range is assigned to Fe–Mg pair from LDH phase. A single backscattering path is applied for the second shell of the other samples. The Fe–Mg distance in 2:1 sample (3.07) (Fig. 2f) is shorter than the $3.11 \text{ \AA}$ and $3.12 \text{ \AA}$ in the 3:1 and 4:1 sample, which agrees with the differences in Me–Mg distance shown in PXRD data and PDF data (Fig. 1f).

The coordination number (CN) of 3.4 for the Fe–Mg distance in the 2:1 sample is much lower than other samples (CN 6–7). This is aligned with the lower R space second shell intensity (Fig. 2e) in the 2:1 sample. The lower CN of Mg–Fe can indicate preferential accumulation of Fe at

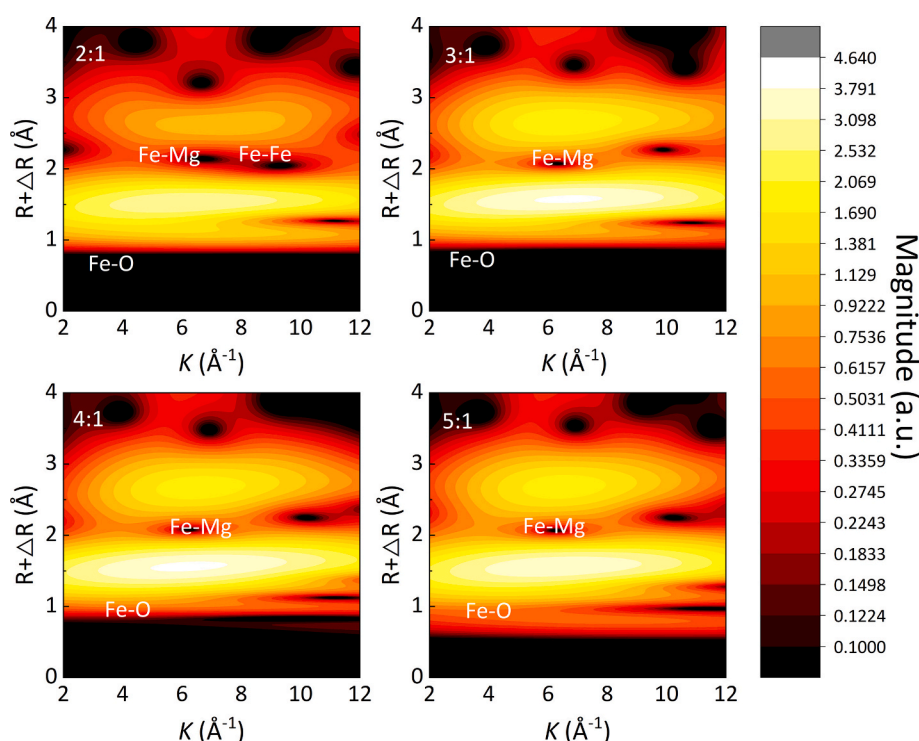


Fig. 3. Wavelet transformation of Fe K-edge EXAFS spectra of Mg-Al/Fe LDHs with M(II)/M(III) ratios from 2:1 to 5:1.

the surface or edge sites in the 2:1 sample, where lower CNs resulted from missing neighboring atoms. In the samples with higher M(II)/M(III) ratio, Fe atoms prefer to be positioned in the bulk sites due to the higher Mg concentration. This phenomenon is further clarified by the higher Al—Fe bulk substitution energy of the 2:1 sample than the samples with higher M(II)/M(III) ratios, as shown in section 3.4.

3.3. Water content in LDH

To determine the precise composition of the LDH phases, thermogravimetric analysis (TGA) was performed to quantify the amount of interlayer water (Fig. 4), which is essential for subsequent molecular modeling of the corresponding phases. Below 100 °C, the observed weight loss is attributed to physically adsorbed water. The first major weight loss, occurring between 100 and 250 °C, corresponds to the removal of interlayer water ($\text{H}_2\text{O}_{\text{Cr}}$), while the second stage, from 250 to 600 °C, is ascribed to the dehydroxylation in the octahedral hydroxide layer ($\text{H}_2\text{O}_{\text{Oh}}$) and the decomposition of interlayer carbonates [13–15]. In the 2:1 sample, which contains $1/5$ of ferrihydrite and $4/5$ of LDH, the 100–250 °C range includes contributions from both the decomposition of $\text{Fe}(\text{OH})_3$ [59] in the temperature range 100–150 °C and the loss of interlayer water from LDH. In contrast, this temperature range in other samples reflects only the removal of interlayer water from the LDH phase. Based on TGA results, the calculated interlayer water contents for the four LDH samples (with varying M(II)/M(III) ratios) are 14.3%, 15.1%, 14.7%, and 13.8%. The total molar ratios of Mg:Al:Fe in the main layer correspond to 4:1.09:0.48, 6:0.89:0.96, 8:0.68:1.21, and 10:0.46:1.46 for the samples 2:1, 3:1, 4:1 and 5:1, respectively, as detailed in section 2.2 and considering $1/5$ of ferrihydrite in the 2:1 sample. Based on these compositions, the number of interlayer water molecules was estimated as 4, 5, 6, and 7 per formula unit (± 0.5). The validity of the molecular models was verified through comparison with theoretical mass loss values from $\text{H}_2\text{O}_{\text{Oh}}$ and interlayer carbonate decomposition, yielding an error margin within $\pm 1.5\%$. The

compositional results were further supported by liquid-phase analysis, showing good consistency between independent methods.

3.4. Ab initio simulations

To gain deeper atomic scale insight into the Fe incorporation mechanism in LDHs with different M(II)/M(III) ratios, DFT calculations were applied. In the simulated models Fe(III) substitutes for Al(III) within the octahedral layers of Mg—Al LDH (Fig. 5a–f). For each composition and Fe content five different structures were optimized, and the probability is given via a Boltzmann distribution (Table S2–S8). The lowest-energy configurations are shown in Fig. 5d–f, and all configurations are demonstrated in Fig. S1–S7. In addition, the magnetic configuration of Fe-containing LDHs was systematically examined. Both ferromagnetic and antiferromagnetic spin arrangements between neighboring Fe(III) centers and the layers were considered. The calculations indicate that the energy difference between antiferromagnetic and ferromagnetic configurations is small and within 0.1%. Given the negligible energetic difference, the antiferromagnetic configuration was adopted in subsequent calculations (Table S9).

To quantify the local environment, bond length distribution and metal-metal distance distributions were also calculated (Fig. S8). The local coordination environment of Fe(III) is highly composition dependent. Although all Fe, Al, and Mg-octahedra share their edges within the main layer, their second coordination shells are distinct. In Mg_2Al_1 , all Fe and Al second shells are in edge-sharing environments (Fig. 5d), and in Mg_3Al_1 , the Fe and Al second shells are in a hybrid sharing mode, both edge-sharing and corner-sharing (Fig. 5e), while in Mg_5Al_1 , there is only corner-sharing in the second coordination shell between trivalent cations (Fig. 5f). The edge-sharing environment at high trivalent-cation content could produce local strain [60] and thus make incorporation less favorable (Fig. 5d & 5e). Moreover, the larger bond length mismatch between Al—O and Fe—O is highly disfavored in edge-sharing environments, which could also potentially restrict the Fe-uptake into Al

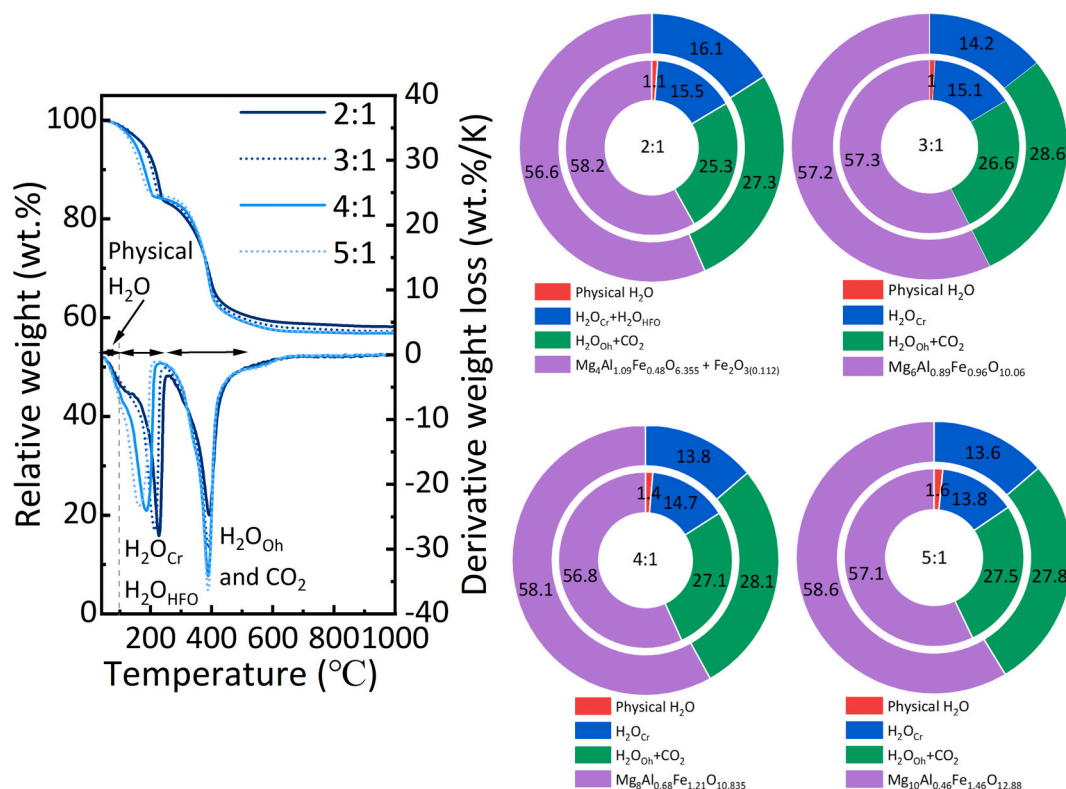


Fig. 4. TG/DTG analysis and compositional determination comparison (wt%) between experiment data (inner ring) with theoretical data (outer ring), for LDHs with M(II)/M(III) ratios from 2:1 to 5:1, and 12.5 mol% Fe(III) among all cations (M(II) + M(III)).

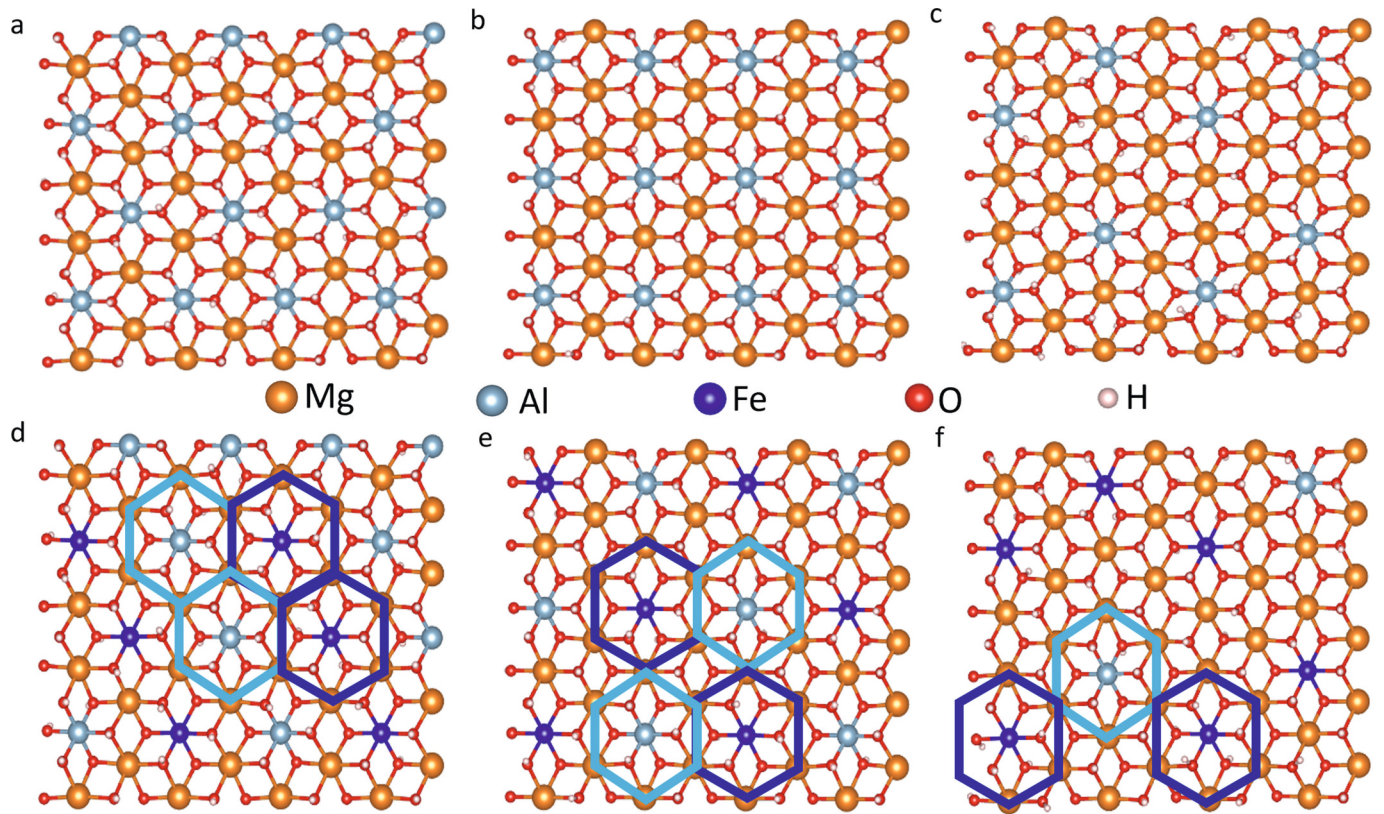


Fig. 5. Optimized structure of (a) Mg_2Al_1 , (b) Mg_3Al_1 , (c) Mg_5Al_1 , (d) $\text{Mg}_2(\text{Al,Fe})_1$, (e) $\text{Mg}_3(\text{Al,Fe})_1$, and (f) $\text{Mg}_5(\text{Al,Fe})_1$. The interlayer and second layer are omitted for clarity. Gold, cyan, blue, red, and white represent the Mg, Al, Fe, O, and H atoms, respectively. The marked hexagons are a schematic illustration for Al and Fe coordination shells. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

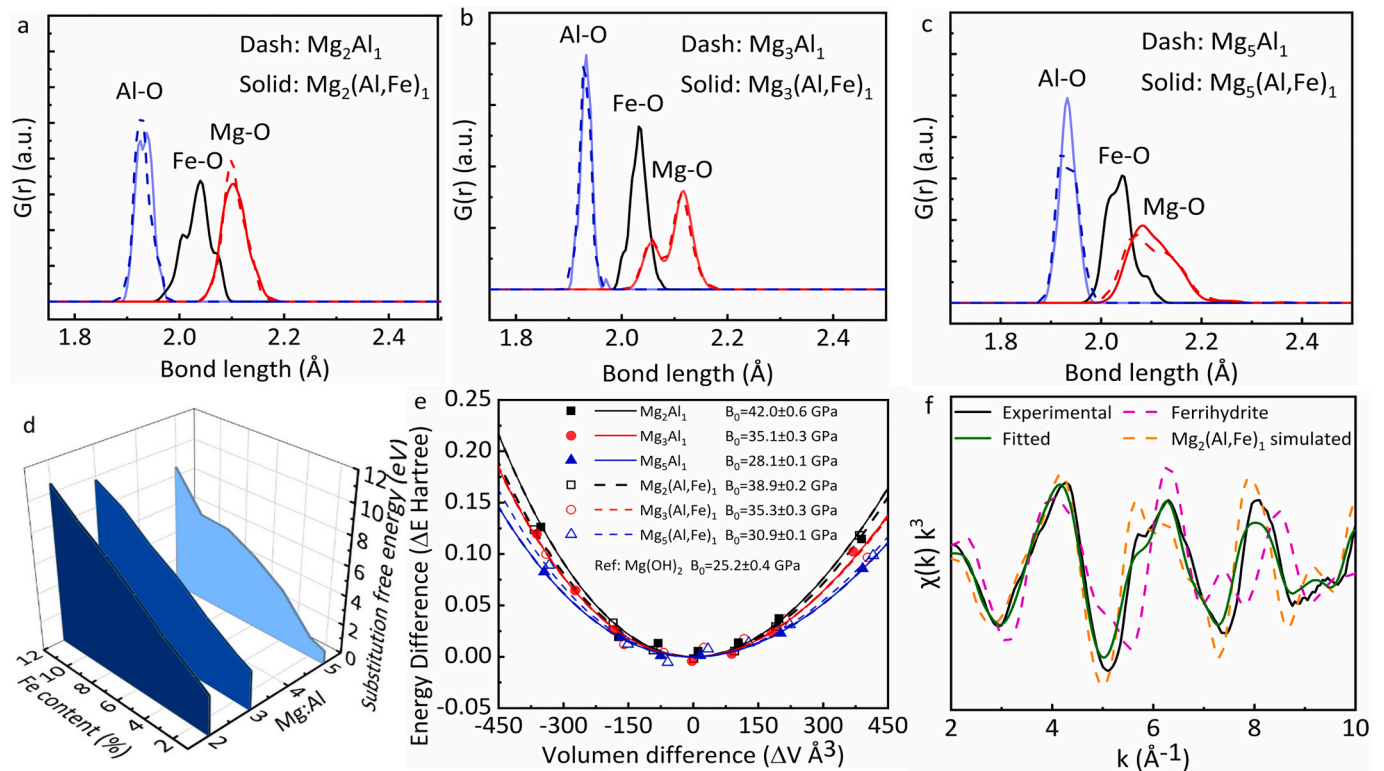


Fig. 6. Bond length distribution function of (a) Mg_2Al_1 and the Fe doped $\text{Mg}_2(\text{Al,Fe})_1$ with an Al to Fe ratio of 5/3, (b) Mg_3Al_1 , and the Fe doped $\text{Mg}_3(\text{Al,Fe})_1$ with a Al to Fe ratio of 1, (c) Mg_5Al_1 and the Fe doped $\text{Mg}_5(\text{Al,Fe})_1$ with an Al to Fe ratio of 1/3, (d) the Fe for Al substitution free energy. (e) Bulk modulus of Mg—Al LDH and reference $\text{Mg}(\text{OH})_2$. (f) Simulated EXAFS spectra of linear combination fitting to the experimental measured spectra.

sites [61]. At higher M(II)/M(III) ratios (Mg_3Al_1 and Mg_5Al_1 , Fig. 5b-c & 5e-f), Fe preferentially occupies Mg-rich neighborhoods, which minimizes lattice distortion, since the Fe—O bond length is closer to Mg—O than to Al—O. These structural observations provide a direct atomic-scale explanation for the experimentally observed difficulty of incorporating Fe in Al-rich LDHs.

This interpretation is also supported by bond length distribution analysis (BDA). In all structures the Fe—O distribution shows a narrow peak centered at ≈ 2.05 Å, indicating that Fe(III) maintains a stable octahedral environment with limited static disorder. A similar phenomenon is observed for Al—O, which also exhibits a narrow peak centered at ≈ 1.93 Å across all ratios. In contrast, the Mg—O distribution is clearly composition-dependent. For Mg_2Al_1 (Fig. 6a), Mg—O exhibits a single peak centered at around 2.10–2.12 Å with modest width, consistent with a relatively uniform Mg environment in the Al-rich lattice, which agrees with the only one type of Mg—Al/Fe edge-edge sharing configuration deciphered by PDF data. For Mg_3Al_1 and Mg_5Al_1 (Fig. 6b-c), however, the Mg—O distribution splits into two distinct peaks: a shorter component at ≈ 2.05 Å and a longer one at ≈ 2.15 Å. The bimodal distribution reflects the existence of two Mg—O environments in Mg-rich LDHs, indicating a structural rearrangement of Mg sites upon increasing Mg to Al ratio, which is consistent with the two types of the interatomic distances (Mg—O—Mg—O—Mg and Al/Fe—O—Mg—O—Al/Fe) determined by PDF data in section 3.1.

Fe substitution further influences both the first and second coordination shells. The cation-cation (second shell) distances increase for all Mg:Al ratios, consistent with the larger ionic radius of Fe(III) compared to Al(III) (Fig. S8). Notably, in Mg_2Al_1 , the Al—Mg peak shape remains nearly unchanged, whereas the Mg—Mg peak broadens upon Fe incorporation (Fig. S8a), which is consistent with the broadening peak at 6.2 Å shown in PDF data. In contrast, for the Mg_3Al_1 and Mg_5Al_1 compositions, the Al—Mg peak undergoes substantial deformation, suggesting a distortion of the hexagonal arrangement within the second coordination shell (Fig. S8b-c). This result implies that, in Mg-richer LDHs, Fe incorporation is accommodated by deformation of the medium-range cation framework, reflecting the greater structural flexibility of these phases. In cementitious systems, such flexibility may favor Fe uptake by LDHs and influence the mechanical properties and stability of the resulting Fe-bearing phases. By contrast, in Al-rich LDHs, Fe incorporation appears to induce more localized strain, which may reduce the capacity of the structure to accommodate further Fe substitution, indicating a lower tolerance of the structure to Fe substitution. In cementitious systems, such effects may lead to the formation of other Fe-bearing phases, potentially supporting passivation layers and favoring long-term durability.

The relatively flexible Mg—O bond (indicated by larger bond length distribution) thus acts as a buffer, effectively compensating the strain induced by heteroatoms (Fe(III)). Interestingly, peak splitting is also observed in the Al—O distribution for $\text{Mg(II)/Al(III)} = 2$ after Fe doping, whereas for $\text{Mg(II)/Al(III)} = 3$ the Al—O peak remains sharp and single. This behavior can be explained by the relative Al/Fe ratio. At $\text{Mg(II)/Al(III)} = 3$, Al and Fe are present in equal numbers, resulting in a more uniform cation distribution. In contrast, at $\text{Mg/Al} = 2$ (Al-rich, $\text{Al(III)/Fe(III)} = 5/3$), the imbalance between Al and Fe leads to a non-uniform local environment and hence peak splitting. In the Mg_5Al_1 composition, Al atoms experience a heterogeneous and asymmetric second cationic shell environment due to the uneven distribution of neighboring metal cations. Due to increasing Fe content (i.e., in $\text{Mg/Al} = 3$ and 5 compositions), Fe replaces Al and becomes the dominate trivalent cation in the phase, the remaining Al compress the neighboring Mg—O bond resulting in a single, well-defined Al—O peak. Contrary, the Fe—O bond in $\text{Mg/Al} = 5$ configuration exhibits a stronger bimodal feature centered around 2.05 Å. This splitting arises from Fe atoms coordinated to oxygen atoms that bridge different neighboring cations, particularly when the adjacent octahedron is occupied by Mg rather than Al (i.e., Fe—O—Mg vs. Fe—O—Al environments). Such heterogeneity in the edge-sharing cationic

environments generates two slightly different Fe—O bond populations, a feature that is less evident in $\text{Mg/Al} = 3$. A weak bimodal feature is also observed in the Fe-doped Mg_2Al_1 system (Fig. 6a), which is contributed by the compression of neighboring Fe. Although Fe is a transition metal and such bond-length variations could in principle arise from a Jahn-Teller distortion, the absence of pronounced peak splitting in $\text{Mg}_3\text{(Al, Fe)}_1$ suggests that the observed Fe—O bimodality originates primarily from variations in the local chemical environment rather than an electronic Jahn-Teller effect. Notably, in the Al-rich case ($\text{Mg(II)/Al(III)} = 2$), the peak at 1.93 Å is more intense than the 1.91 Å peak, whereas in the Fe-rich case ($\text{Mg(II)/Al(III)} = 5$) the reverse is observed. This suggests a redistribution of Al—O bond lengths depending on whether Fe is present in minority or majority, reflecting the different ways in which Fe perturbs the local structure. Despite these variations, the Fe—O bond itself remains consistent at 2.0–2.1 Å across all ratios (Fig. 6a-c). Such bimodality is also observed in the second coordination shell. The Al—Mg distance also demonstrates a peak splitting upon Fe-substitution in Mg_3Al_1 and Mg_5Al_1 (Fig. S8b-c), further demonstrating that Fe incorporation perturbs not only the first-shell M—O bonding but also the medium-range cationic ordering.

The substitution free energy is calculated for the energetically lowest configuration for each Mg/M(III) ratio. The calculated substitution energies further emphasize this compositional effect (Fig. 6d). The Al—Fe exchange energy is highest for Mg_2Al_1 , followed by Mg_3Al_1 and Mg_5Al_1 , demonstrating that Fe incorporation is most unfavorable in Al-rich LDHs and progressively more favorable in Mg-rich environments. The higher Al—Fe exchange energy for Mg_2Al_1 agrees with the Fe accumulation preference at edge or surface sites in Mg—Al LDH with lower M(II)/M(III) as inferred from the EXAFS results presented in section 3.2. The energetic penalty observed at elevated Al concentrations is attributed to the formation of edge-sharing M(III)-centered octahedra, which increases short-range electrostatic repulsion and imposes significant local octahedral strain [60]. At higher Mg to Al ratios, Fe is surrounded predominantly by more flexible Mg(II), reducing electrostatic repulsion and lattice distortion, and thereby lowering the incorporation energy. These trends reflect the experimentally observed Fe uptake behavior derived from the combined Fe K-edge EXAFS/XANES analyses (section 3.2), in which Fe incorporation is suppressed at $\text{Mg/Al} = 2$ due to the presence of ferrihydrite-like impurity phases, but becomes progressively more favorable at higher Mg/Al ratios.

Bulk modulus calculation shows a clear dependence on composition and is strongly influenced by Fe substitution (Fig. 6e). Among the compositions studied, Mg_2Al_1 exhibits the highest bulk modulus (42 GPa), while Mg_5Al_1 is the most compressible (28 GPa). This trend can be rationalized by the different bonding environments: the higher fraction of Al—O octahedra in Mg_2Al_1 provides shorter, stiffer bonds that resist compression, whereas the dominance of longer, more flexible Mg—O bonds in Mg_5Al_1 makes the lattice softer. After Fe doping, however, the composition dependency of bulk modulus changes: Mg_2Al_1 becomes softer, Mg_5Al_1 becomes harder, and Mg_3Al_1 remains nearly unchanged (Fig. 6b). In Mg_2Al_1 , a slight shift to shorter Al—O bond length is observed (Fig. 6a). This does not strengthen the lattice, but instead reflects a distortion caused by the size mismatch between Fe(III) and Al(III) (Fe—O ≈ 2.05 Å vs. Al—O ≈ 1.91 Å). Incorporation of the larger Fe(III) expands its local octahedral environment and forces adjacent Al—O octahedra to compress, creating a local strain [16]. This pre-strained structure reduces the ability of the lattice to resist external pressure, thereby lowering the bulk modulus. In pure Mg_5Al_1 , due to flexible Mg—O bonds and stiff Al—O octahedra, pure Mg_5Al_1 can be effectively compressed or relaxed. As Fe—O bond lengths are closer to Mg—O than to Al—O, Fe-doping induces a slight adjusting of Mg—O bonds (right shift from 2.05 to 2.07 Å, Fig. 6c), which enhances the lattice resistance to external pressure and increases the bulk modulus. In Mg_3Al_1 , where Al and Fe are present in roughly equal amounts, no significant change in bond lengths is observed and the bulk modulus remains nearly constant. Taken together, these results show that Fe(III) acts as a lattice softener in

Al-rich LDHs, a stiffener in Mg-rich LDHs, and has minimal impact in intermediate compositions. The contrasting effect of Fe(III) incorporation on the bulk modulus of Al-rich and Mg-rich LDHs may have implications for the mechanical behavior of interfacial passivation layers. In Al-rich LDHs, Fe-induced lattice softening could enhance stress accommodation and improve interfacial strain compatibility, whereas in Mg-rich LDHs, lattice stiffening may result in a more rigid structure. These atomic-scale elastic trends may influence the mechanical response of the passivation layer; however, their macroscopic consequences require further investigation.

Importantly, all LDH phases retain a higher bulk modulus than brucite ($\text{Mg}(\text{OH})_2$), underscoring the reinforcing role of trivalent cations (Al and Fe) in layered hydroxide frameworks compared to the purely divalent brucite ($B_0 \approx 25$ GPa). To this end, we believe that in general the less compressible trivalent cations act as a framework for stiffness of LDHs. Due to the highly anisotropic nature of LDHs, the bulk modulus calculations here provide an approximation of the elastic behavior of LDH. Given the strong dependence of in-plane elasticity on composition and structure [62–65], directional elastic calculations were performed to isolate the intrinsic in-plane mechanical response of the LDH layers. The resulting in-plane Young's modulus for Mg_2Al_1 , Mg_3Al_1 , and Mg_5Al_1 are 123, 122, and 101 GPa, respectively, whereas the corresponding Fe-substituted systems ($\text{Mg}_2(\text{Fe},\text{Al})_1$, $\text{Mg}_3(\text{Fe},\text{Al})_1$, and $\text{Mg}_5(\text{Fe},\text{Al})_1$) exhibit in-plane Young's moduli of 120, 107, and 98 GPa, respectively. These values are significantly larger than the corresponding bulk modulus, confirming the pronounced stiffness of the metal-oxygen framework within the LDH layers (Table S10). Both pristine and Fe-substituted systems follow a similar compositional trend, with increasing M(III) content leading to enhanced in-plane stiffness, while Fe substitution induces a slight reduction in the in-plane Young's modulus. Interestingly, in Mg_5Al_1 the addition of Fe increases the bulk modulus while the in-plane Young's modulus decreases slightly. This apparent discrepancy reflects the strongly anisotropic elastic response of LDHs: whereas the bulk modulus is governed by volumetric compression involving both interlayer spacing and metal-oxygen bonds, the in-plane Young's modulus probes the rigidity of the metal-hydroxide framework within individual layers. Furthermore, the in-plane shear modulus G (in-plane) exhibits a similar compositional trend but is an order of magnitude larger than the interlayer shear modulus $G(\text{inter-layer})$ (Table S10), highlighting the mechanically layered nature of LDHs with strong in-plane bonding and weak resistance to interlayer sliding.

Comparison of simulated EXAFS with experimental EXAFS provides important validation. Simulated spectra for the ideal $\text{Mg}_2(\text{Al},\text{Fe})_1$ structure shows oscillations distinct from those measured experimentally, instead, resembling the spectra of $\text{Mg}(\text{II})/\text{Al}(\text{III}) \geq 3$ LDHs (Fig. 2d & Fig. 6f). This discrepancy indicates that Fe is not successfully incorporated into the Mg_2Al_1 LDH. To reproduce the experimental $\text{Mg}_2(\text{Al},\text{Fe})_1$ spectrum (Fig. 2d), we performed linear combination fitting using the simulated $\text{Mg}_2(\text{Al},\text{Fe})_1$ spectrum and measured ferrihydrite spectra. The best fit yielded a composition of 81% LDH and 19% ferrihydrite. This confirms that in Al-rich compositions, a fraction of the Fe remains outside the LDH lattice and participating in ferrihydrite, consistent with both experimental and theoretical predictions.

4. Conclusions

The corrosion and passivation of reinforcing steel in low-carbon cements with high Mg content is becoming a matter of concern. The lower pH of these binders compared to Portland cements can accelerate the oxidation of Fe^0 , and the dissolution and diffusion of Fe(II) and Fe(III) away from the steel surface, leading to faster corrosion [27]. LDH phases generated during low-carbon cement hydration have been reported to accommodate Fe(III) within their octahedral layers [13,66]. This incorporation provides an alternative sink for Fe(III) and may reduce the fraction of Fe(III) available for the growth of dense iron (hydr)oxide passivation layers. By systematically investigating the Fe(III)

incorporation capability of LDHs as a function of composition and local structural environment through integrating synchrotron-based spectroscopy and diffraction with first-principles calculations, this study establishes a direct link between cation distribution, bond-length heterogeneity, energetics, and mechanical response in Fe(III)-bearing LDHs, offering theoretical guidance for improving the durability of low-carbon cementitious systems.

These results demonstrate that Fe incorporation into LDH phases is not an intrinsic stabilizing mechanism, but is strongly governed by lattice tolerance and local structural adaptability. At trivalent-cation-rich compositions, the LDH framework is unable to accommodate Fe(III) without inducing significant local strain, leading to the preferential formation of iron (hydr)oxide phases. In contrast, Mg-rich LDHs promote structural softening and heterogeneous bonding environments that facilitate complete Fe(III) incorporation into the LDH lattice. The energetic favorability of Fe incorporation leads to Fe-bearing LDHs with increased compositional flexibility. In summary, these findings offer suggestions for controlling Fe incorporation into LDH phases. Given the intrinsic formation of LDH phases in low-carbon, Mg-rich cement systems, the results offer transferable insights into how LDH composition may influence interfacial phase assemblages relevant to steel protection.

In addition to the Mg/Al ratio in the solid phase, pore solution chemistry would also be expected to play a key role in governing the kinetics and pathways of Fe(III) incorporation into LDHs. High pH conditions typical of cement pore solutions favor LDH formation and Fe(III) incorporation [14]. Furthermore, dissolved silicate species can interact with Fe(III), forming a soluble iron-silicon complex [67] and lowering the Fe(III) incorporation in the main layer of LDH, potentially modifying nucleation pathways and incorporation mechanisms. In the present study, a simplified approach is intentionally adopted, focusing on well-defined solid-phase cation ratios as a first step toward understanding the fundamental mechanisms. Such single-phase systems provide a necessary basis for isolating key interactions. The influence of pore solution chemistry, although not explicitly addressed here, will be incorporated in future work to progressively increase the system complexity and better approximate real cement environments.

This study primarily focuses on the factors governing the incorporation of Fe(III) in LDH structure. However, during the early stages of steel corrosion, significant amounts of Fe(II) are also present. The role of Fe(II) is not considered in the present work to maintain a controlled and mechanistic investigation of Fe(III)-related processes. Future studies will extend this approach by exploring the incorporating Fe(II) in LDH based on experiment and simulation methods.

CRediT authorship contribution statement

Jiaying Ban: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ruotao Yang:** Writing – original draft, Validation, Methodology, Investigation. **Sergey V. Churakov:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization. **Barbara Lothenbach:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization. **John L. Provis:** Writing – review & editing, Supervision, Methodology, Data curation, Conceptualization. **Kaifeng Wang:** Writing – review & editing, Validation, Resources. **Haixing Fang:** Writing – review & editing, Resources, Formal analysis, Data curation. **Bin Ma:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge the Swiss National Science Foundation (SNSF project no. 200021_213078, SNSF Advanced grant no. TMAG-2_209222, and SNSF Sinergia grant no. 10000099) and the Open Fund of State Key Laboratory of Nuclear Power Safety Technology and Equipment (SKL-2025-TS-09). Experiments were performed at BL22 CLÆSS beamline at ALBA Synchrotron (proposal ID 2024028190) with the collaboration of Dr. Oleg Usoltsev and other ALBA staff. We also acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at P65 Beamline. Data was collected using an ionization chamber provided by DESY Photon Science. We would like to thank Dr. Edmund Welter for assistance during the experiments. Beamtime was allocated for proposal ID I-20240191 EC. Experiments were performed on the SAMBA beamline using the chemistry lab for support at SOLEIL Synchrotron, France (proposal ID 20231591). We are grateful to Dr. Fonda Emiliano for assistance and to the SOLEIL staff for smoothly running the facility. We also acknowledge the European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities under proposal number (IH-CH-1858). The authors acknowledge Zeyu Zhou from Empa, Dr. Dengquan Wang and Dr. Davide Ferri from PSI for the TGA, ICP-OES, and UV-VIS measurements. The authors acknowledge Swiss National Supercomputing Centre (CSCS) for granting computing resources on Alps-Daint supercomputer (project lp66).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cemconres.2026.108270>.

Data availability

Data will be made available on request.

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