

Evidence of Multiple Sorption Modes in Layered Double Hydroxides Using Mo As Structural Probe

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▶ To cite this version:

Bin Ma, Alejandro Fernandez-Martinez, Sylvain Grangeon, Christophe Tournassat, Nathaniel Findling, et al.. Evidence of Multiple Sorption Modes in Layered Double Hydroxides Using Mo As Structural Probe. Environmental Science and Technology, 2017, 51 (10), pp.5531 - 5540. 10.1021/acs.est.7b00946 . hal-01849363

HAL Id: hal-01849363 https://brgm.hal.science/hal-01849363

Submitted on 28 Jun 2022

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Supporting Information

2	Evidence of multiple sorption modes in layered
3	double hydroxides using Mo as structural probe
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19	The Supporting Information contains 21 pages, 2 texts, 7 tables and 13 figures.

20 Text S1. Characterization of Synthesized CaAl LDHs.

Freshly synthesized Cl⁻ and SO₄²⁻ CaAl LDHs have well-crystallized hexagonal-shaped plate morphology (Figure S2) but different average sizes: around \emptyset 0.5 µm for AFm-Cl₂ and \emptyset 5 µm AFm-SO₄, respectively. The specific surface areas and the average edge lengths thus differ (Table S6), with lateral surface (S₁) area concentrations equal for AFm-Cl₂ and AFm-SO₄ to 2.19×10¹⁸ and 2.29×10¹⁷ nm² g⁻¹, respectively, as obtained from¹:

$$S_l = \frac{P}{S \times \rho} \tag{1}$$

where *P*, *S*, and ρ represent CaAl LDHs particle's perimeter (nm), basal plane surface area (nm²), and density (g nm⁻³), respectively.

29 X-ray diffraction (XRD) was used to determine the nature and amount of eventual impurities 30 and the inter-layer distances of the synthesized CaAl LDHs (Figure S1), including AFm-SO₄, AFm-Cl₂, and AFm-CO₃. Due to the sulfate-deficiency during the synthesis, no ettringite was 31 32 formed in the fresh AFm-SO₄, but katoite [Ca₃Al₂(OH)₁₂] was observed as an impurity. AFm-SO₄ and AFm-Cl₂ powders were also characterized after 7 days in equilibrium with N₂-33 saturated water at pH 12.4. The (003) inter-layer distance of AFm-SO₄, was initially 34 8.128±0.006 Å at 5% relative humidity (RH) corresponding to 10.5 H₂O hydration state², and 35 it changed to a shorter distance of 7.884 \pm 0.006 Å with time. The lack of SO₄²⁻ is compensated 36 37 with OH⁻ in the inter-layer space, resulting in the formation of AFm-OH with 13 H₂O molecules². Besides, a tiny diffraction peak occurred at 11.65° after equilibration of AFm-SO₄ 38 39 in water, which is probably derived from gypsum formed during sample drying. A strict N₂ 40 protection gives us confidence to exclude formation of AFm-CO₃ (i.e., CO₂ contamination) in 41 both reacted AFm-SO₄ and AFm-Cl₂. No detectable impurity is observed with the AFm-Cl₂ 42 phase, characterized by an inter-layer distance of 7.838±0.006 Å.

43 Atomic ratios between each element in CaAl LDHs were estimated by digesting 100 mg CaAl 44 LDHs solid phase in a certain amount of 1% HNO₃, and by measuring total aqueous Ca, Al, and S concentrations using inductively coupled plasma optical emission spectrometry (ICP-45 OES). This nitrolysis method was applied for each CaAl LDH in duplicate. Katoite impurity 46 47 in AFm-SO₄ was inferred from the Ca/Al stoichiometry. Structural water content was 48 determined by thermal gravimetric analysis (TGA) and derivative thermogravimetric analysis 49 (DTG) curves (Figure S9) and dehydration and dehydroxylation were included in the total water loss till 700 °C³, at which temperature the water loss is assumed to be completed. Based 50 51 on the calculation, 78 at.% AFm-SO₄ and 22 at.% katoite composed the product for AFm-SO₄ synthesis. The experimental chemical formula of AFm-SO₄ and AFm-Cl₂ were 52 53 $Ca_4Al_2O_6(SO_4)_{0.92}(OH)_{0.08} \cdot 6.4H_2O$ and $Ca_4Al_2O_6Cl_{1.64}(OH)_{0.36} \cdot 7.4H_2O$, respectively.

55 The released Cl⁻ is more than the stoichiometric amount that may be derived from the corrosion of double-layer structure. This is confirmed by the newly appearance of a katoite 56 57 diffraction peak for Mo-reacted samples in the synchrotron based XRD patterns since sample ClA (Figure S8), in agreement with saturation index (SI) computed from the aqueous phase 58 composition after reaction of both CaAl LDHs with molybdate for 48 h (Figure S10). 59 60 Molybdate could also affect heavily the metastability of AFm-SO₄ and result in ettringite 61 formation (Figure S8). Compared to the dissolution products for 7 days (Figure S1), phases 62 transformation seems to be promoted under the effect of molybdate. Indeed, the pair 63 distribution function (PDF) analysis of high energy XRD data conducted on six selected 64 sorption products, and compared to the calculated PDF patterns of katoite, ettringite, and 65 powellite, shows almost no apparent phase transformation, except the formation of katoite and 66 ettringite in Mo-reacted AFm-Cl₂ and AFm-SO₄, respectively (Figure S11 and Figure S12).



68 69 **Figure S1.** X-ray diffraction patterns of fresh CaAl LDHs and the phases after dissolution.

70 The dissolution equilibrium was set at pH \sim 12.4 for 7 days and samples were mounted

71 oriented at relative humidity of 5%. Cu Kα radiation at 1.5406 Å is used.



73 Figure S2. FE-SEM micrographs of the synthesized CaAl LDHs. Scale bar, 5 μm. (a) Pristine

74 AFm-SO₄ particles. (b) Pristine AFm-Cl₂ particles.

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Figure S3. Concentration variation profile of aqueous MoO_4^{2-} and Cl⁻ as a function of molybdate loading on AFm-Cl₂. The change in concentration of adsorbed MoO_4^{2-} is plotted

by the black solid dots and the released Cl⁻ is represented by the red hollow dots. The

80 theoretical [Cl⁻]_{released} is estimated by a stoichiometric anion exchange, shown as the blue

81 curve. The selected three adsorption products are marked by A, B, and C.





Figure S4. PHREEQC modelling results as a function of $[Mo(VI)]_{aq}$ in equilibrium. (a)

Dominated solid speciation in AFm-Cl₂ reactors. (b) Dominated solid speciation in AFm-SO₄
reactors. (c) Modelling results of aqueous Ca, Al, and Cl concentrations in AFm-Cl₂ reactors.
(b) Modelling results of aqueous Ca, Al, and S concentrations in AFm-SO₄ reactors. Reactors,

87 marked by A to F, correspond to the same ones in Figure 1.



Figure S5. In-situ time resolved XRD patterns of reacted AFm-Cl₂ at each loading step. The diffraction peak range of layer-to-layer distance (d_{002}), circled by red dotted lines, is enlarged in the main text to provide more details. The Cl₂/MoO₄ ratio at each step is shown following the sample name. The main phase of ClF_t is AFm-MoO₄, with no obvious signal of katoite and powellite observed.

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Figure S6. In-situ time resolved XRD patterns of reacted AFm-SO₄ at each loading step. The diffraction peak range of layer-to-layer distance (d_{003}), circled by red dotted lines, is enlarged in the main text to provide more details. The SO₄/MoO₄ ratio at each step is shown following the sample name.



Figure S7. Calculated Mo K-edge XANES spectra of different Mo coordination. From the
bottom up, the pre-edge intensity decreases steadily and the molybdate coordination
environments are pure O.C. (octahedral Mo(VI)-katoite, both inner-incorporated and edgeincorporated), distorted O.C. (octahedral Mo(VI)-AFm phases, both the substitution and
epitaxial growth), distorted T.C. (Ca-MoO₄ ion pair, both the substitution and epitaxial

- 110 growth for tetrahedral Mo(VI)-AFm phases), and pure T.C. (CaMoO₄ and Na₂MoO₄). O.C
- and T.C. represent octahedral coordination and tetrahedral coordination, respectively.





Figure S8. Synchrotron based X-ray diffraction patterns of the selected adsorption products

115 for CaAl LDHs. Inter-layer peaks are located in the range of $2 - 4^{\circ}$.



Figure S9. Thermogravimetric analyses of the synthesized CaAl LDHs. (a) AFm-SO₄ phase.





Figure S10. Saturation index of several possibly formed mineral phases as a function of
[Mo(VI)]_{initial}. (a) For AFm-Cl₂ system. (b) For AFm-SO₄ system. Calculation is based on the
aqueous data in batch sorption experiment on CaAl LDHs.



Figure S11. Comparison of calculated and experimental PDF of katoite, powellite, and AFmCl₂ samples in batch sorption experiment. The grey dotted line is the subtracted signal of ClC

132 on fresh AFm-Cl₂.



Figure S12. Comparison of calculated and experimental PDF of katoite, powellite, ettringite
and AFm-SO₄ samples in batch sorption experiment. The grey dotted line is the subtracted
signal of SC on fresh AFm-SO₄.





- 139 Figure S13. Schematic representation of the meaning of LS and LEP in LDHs. LS and LEP
- 140 represent lateral surface and lateral edge perimeter, respectively.

- х T .

157	Table S1. Solution content of selected elements for AFm-Cl ₂ experiments before introducing
158	MoO_4^{2-} . Concentrations were determined after reaching dissolution equilibrium, which was
159	confirmed by dissolution kinetics ^{<i>a</i>} .

	aII	[Ca] _{aq}	[Al] _{aq}	[Cl] _{aq}
ID	рп	$/mol L^{-1}$	$/mol L^{-1}$	/mol L ⁻¹
ClA	12.37	6.23(6)×10 ⁻³	3.25(1)×10 ⁻³	4.49(21)×10 ⁻³
	nd	6.31(7)×10 ⁻³	3.25(2)×10 ⁻³	4.54(21)×10 ⁻³
	nd	6.43(7)×10 ⁻³	3.25(2)×10 ⁻³	4.59(22)×10 ⁻³
ClB	nd	6.24(7)×10 ⁻³	3.26(2)×10 ⁻³	4.64(21)×10 ⁻³
	nd	6.36(8)×10 ⁻³	3.22(2)×10 ⁻³	4.76(23)×10 ⁻³
	nd	6.31(7)×10 ⁻³	3.29(3)×10 ⁻³	4.63(21)×10 ⁻³
	nd	6.35(6)×10 ⁻³	3.29(3)×10 ⁻³	4.64(23)×10 ⁻³
	nd	6.26(7)×10 ⁻³	3.24(1)×10 ⁻³	4.58(22)×10 ⁻³
	nd	6.28(6)×10 ⁻³	3.27(2)×10 ⁻³	4.74(21)×10 ⁻³
ClC	nd	6.28(6)×10 ⁻³	3.27(1)×10 ⁻³	4.79(23)×10 ⁻³

^a nd: not determined; Uncertainties from three times repeated analyses of identical samples
 are given by the number in brackets on the last digit(s).

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Table S2. Solution content of selected elements for AFm-Cl2 experiments after equilibrium176with MoO_4^{2-} for 48 h^a.

ID	ъU	[Mo] _{aq}	q	[Ca] _{aq}	[Al] _{aq}	[Cl] _{aq}
ID	рп	/mol L ⁻¹	$/mol g^{-1}$	/mol L ⁻¹	/mol L ⁻¹	/mol L ⁻¹
ClA	12.37	1.42(17)×10 ⁻⁷	3.93(42)×10 ⁻⁷	6.30(10)×10 ⁻³	3.07(4)×10 ⁻³	4.55(21)×10 ⁻³
	nd	1.02(12)×10 ⁻⁷	9.57(51)×10 ⁻⁷	6.32(8)×10 ⁻³	3.00(2)×10 ⁻³	4.58(21)×10 ⁻³
	nd	1.89(18)×10 ⁻⁷	1.97(13)×10 ⁻⁶	6.19(7)×10 ⁻³	2.82(2)×10 ⁻³	4.73(22)×10 ⁻³
ClB	12.37	2.14(8)×10 ⁻⁷	2.47(16)×10 ⁻⁶	6.29(8)×10 ⁻³	2.99(3)×10 ⁻³	4.80(22)×10 ⁻³
	nd	3.43(3)×10 ⁻⁷	3.98(21)×10 ⁻⁶	6.25(6)×10 ⁻³	2.88(1)×10 ⁻³	4.90(22)×10 ⁻³
	nd	5.91(7)×10 ⁻⁷	4.98(32)×10 ⁻⁶	6.18(6)×10 ⁻³	2.88(1)×10 ⁻³	4.83(22)×10 ⁻³
	nd	6.74(13)×10 ⁻⁷	5.98(30)×10 ⁻⁶	6.15(8)×10 ⁻³	2.82(2)×10 ⁻³	4.76(22)×10 ⁻³
	nd	5.75(16)×10 ⁻⁷	7.43(38)×10 ⁻⁶	6.28(6)×10 ⁻³	3.06(1)×10 ⁻³	4.76(22)×10 ⁻³
	nd	8.51(16)×10 ⁻⁷	8.93(40)×10 ⁻⁶	6.28(6)×10 ⁻³	3.04(1)×10 ⁻³	5.06(23)×10 ⁻³
ClC	12.37	1.21(1)×10 ⁻⁶	9.92(44)×10 ⁻⁶	6.28(6)×10 ⁻³	3.03(2)×10 ⁻³	5.07(23)×10 ⁻³
ClD	12.38	3.98(32)×10 ⁻⁶	1.35(4)×10 ⁻⁴	5.83(15)×10 ⁻³	3.10(7)×10 ⁻³	nd
ClE	12.38	4.05(28)×10 ⁻⁶	2.60(7)×10 ⁻⁴	5.68(19)×10 ⁻³	3.02(5)×10 ⁻³	nd
ClF	12.37	1.59(13)×10 ⁻³	1.52(7)×10 ⁻³	2.27(7)×10 ⁻³	1.44(4)×10 ⁻³	9.35(16)×10 ⁻³
ClG	12.41	1.03(5)×10 ⁻³	3.90(9)×10 ⁻³	8.15(16)×10 ⁻⁴	4.93(12)×10 ⁻³	nd
ClH	12.42	7.50(35)×10 ⁻³	6.14(21)×10 ⁻³	8.97(36)×10 ⁻⁵	7.86(23)×10 ⁻³	nd

^a nd: not determined; Uncertainties from three times repeated analyses of identical samples

178 are given by the number in brackets on the last digit(s).

187	Table S3. Solution content of selected elements for AFm-SO4 experiments before introducing
188	MoO_4^{2-} . Concentrations were determined after reaching dissolution equilibrium, which was
189	confirmed by dissolution kinetics ^{<i>a</i>} .

ID	nII	[Ca] _{aq}	[Al] _{aq}	[S] _{aq}
ID	рп	$/mol L^{-1}$	$/mol L^{-1}$	/mol L ⁻¹
SA	12.35	2.69(3)×10 ⁻³	1.97(2)×10 ⁻³	5.08(22)×10 ⁻⁵
	nd	2.74(4)×10 ⁻³	1.97(2)×10 ⁻³	5.32(17)×10 ⁻⁵
	nd	2.77(3)×10 ⁻³	1.96(1)×10 ⁻³	5.08(26)×10 ⁻⁵
SB	nd	2.70(3)×10 ⁻³	1.98(1)×10 ⁻³	5.13(14)×10 ⁻⁵
	nd	2.73(3)×10 ⁻³	1.97(2)×10 ⁻³	4.88(29)×10 ⁻⁵
	nd	2.74(3)×10 ⁻³	1.97(1)×10 ⁻³	4.98(24)×10 ⁻⁵
	nd	2.68(2)×10 ⁻³	1.89(1)×10 ⁻³	6.04(16)×10 ⁻⁵
	nd	2.71(3)×10 ⁻³	1.96(1)×10 ⁻³	5.00(5)×10 ⁻⁵
	nd	2.72(3)×10 ⁻³	1.95(2)×10 ⁻³	4.93(24)×10 ⁻⁵
SC	nd	2.74(3)×10 ⁻³	1.97(2)×10 ⁻³	5.02(44)×10 ⁻⁵

^a nd: not determined; Uncertainties from three times repeated analyses of identical samples
 are given by the number in brackets on the last digit(s).

Table S4. Solution content of selected elements for AFm-SO₄ experiments after equilibrium with MoO_4^{2-} for 48 h^{*a*}.

ID nH		[Mo] _{aq}	q	[Ca] _{aq}	[Al] _{aq}	$[S]_{aq}$
ID	рн	/mol L ⁻¹	/mol g ⁻¹	/mol L ⁻¹	/mol L ⁻¹	/mol L ⁻¹
SA	12.34	8.75(90)×10 ⁻⁷	2.62(3.04)×10 ⁻⁸	2.77(3)×10 ⁻³	$1.95(2) \times 10^{-3}$	6.00(17)×10 ⁻⁵
	nd	1.90(11)×10 ⁻⁶	5.61(3.67)×10 ⁻⁸	2.80(3)×10 ⁻³	1.97(2)×10 ⁻³	5.11(13)×10 ⁻⁵
	nd	3.96(26)×10 ⁻⁶	8.76(9.20)×10 ⁻⁸	2.65(3)×10 ⁻³	1.85(1)×10 ⁻³	6.09(4)×10 ⁻⁵
SB	12.35	4.88(35)×10 ⁻⁶	1.39(1.18)×10 ⁻⁷	2.74(3)×10 ⁻³	1.92(1)×10 ⁻³	5.21(4)×10 ⁻⁵
	nd	7.86(49)×10 ⁻⁶	2.21(1.59)×10 ⁻⁷	2.78(4)×10 ⁻³	1.94(3)×10 ⁻³	5.19(17)×10 ⁻⁵
	nd	9.70(6)×10 ⁻⁶	4.22(2.25)×10 ⁻⁷	2.68(3)×10 ⁻³	1.86(1)×10 ⁻³	5.95(9)×10 ⁻⁵
	nd	1.23(8)×10 ⁻⁵	1.85(2.20)×10 ⁻⁷	2.77(4)×10 ⁻³	1.88(3)×10 ⁻³	1.29(2)×10 ⁻⁴
	nd	1.43(8)×10 ⁻⁵	5.89(2.84)×10 ⁻⁷	2.79(4)×10 ⁻³	1.98(2)×10 ⁻³	4.27(9)×10 ⁻⁵
	nd	1.73(6)×10 ⁻⁵	7.29(2.58)×10 ⁻⁷	2.77(4)×10 ⁻³	1.96(2)×10 ⁻³	4.44(9)×10 ⁻⁵
SC	12.34	1.94(5)×10 ⁻⁵	8.17(2.51)×10 ⁻⁷	2.77(3)×10 ⁻³	1.95(1)×10 ⁻³	4.45(3)×10 ⁻⁵
SD	12.35	2.07(12)×10 ⁻⁴	3.30(49)×10 ⁻⁵	2.37(6)×10 ⁻³	1.81(4)×10 ⁻³	5.41(86)×10 ⁻⁵
SE	12.36	2.84(17)×10 ⁻⁴	1.20(8)×10 ⁻⁴	2.28(8)×10 ⁻³	1.88(7)×10 ⁻³	5.98(50)×10 ⁻⁵
SF	12.41	2.66(13)×10 ⁻³	9.81(72)×10 ⁻⁴	1.18(3)×10 ⁻³	2.71(8)×10 ⁻³	2.65(22)×10 ⁻⁴
SG	12.40	2.45(15)×10 ⁻³	3.19(10)×10 ⁻³	4.07(9)×10 ⁻⁴	6.10(21)×10 ⁻³	7.56(60)×10 ⁻⁴
SH	12.42	7.63(42)×10 ⁻³	6.07(22)×10 ⁻³	1.02(4)×10 ⁻⁴	8.04(26)×10 ⁻³	2.77(4)×10 ⁻³

^a nd: not determined; Uncertainties from three times repeated analyses of identical samples are given by the number in brackets on the last digit(s).

213	Table S5.	Equilibrium	constants	of selected	phases ^a	and reactions	occurred on	CaAl LDHs at
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each sorption stage. logK values of AFm edge sites sorption and AFm-MoO₄ formation were

adapted.

	Equation	logK
Solubility equilibrium		
AFm-Cl ₂	$\begin{aligned} Ca_4Al_2Cl_2(OH)_{12} \cdot 4H_2O + 12H^+ &\Leftrightarrow 4Ca^{2+} + \\ 2Al^{3+} + 2Cl^- + 16H_2O \end{aligned}$	74.93
AFm-SO ₄	$\begin{aligned} \mathrm{Ca}_{4}\mathrm{Al}_{2}(\mathrm{SO}_{4})(\mathrm{OH})_{12}\cdot 6\mathrm{H}_{2}\mathrm{O} + 12\mathrm{H}^{+} &\Leftrightarrow 4\mathrm{Ca}^{2+} \\ & + 2\mathrm{Al}^{3+} + \mathrm{SO}_{4}^{2-} + 18\mathrm{H}_{2}\mathrm{O} \end{aligned}$	73.07
AFm-MoO ₄	$Ca_{4}Al_{2}(MoO_{4})(OH)_{12} \cdot 4H_{2}O + 12H^{+} \Leftrightarrow$ $4Ca^{2+} + 2Al^{3+} + MoO_{4}^{2-} + 16H_{2}O$	74.00
CaMoO ₄	$CaMoO_{4(s)} \Leftrightarrow Ca^{2+} + MoO_4^{2-}$	-7.90
Katoite(C ₃ AH ₆)	$Ca_{3}Al_{2}(OH)_{12} + 12H^{+} \Leftrightarrow 3Ca^{2+} + 2Al^{3+} + 12H_{2}O$	80.32
Ettringite	$Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12} \cdot 26H_{2}O + 12H^{+} \Leftrightarrow$ $6Ca^{2+} + 2Al^{3+} + 3SO_{4}^{2-} + 38H_{2}O$	56.97
Sorption stage		
Edge sorption	$2AFm_edge-OH + MoO_4^{2-} \Leftrightarrow$ $(AFm_edge)_2-MoO_4 + 2OH^{-1}$	2.80 ^b , 1.05 ^c
AFm-MoO ₄ formation	$4Ca^{2+} + 2Al^{3+} + MoO_4^{2-} + 16H_2O \Leftrightarrow$ $Ca_4Al_2(MoO_4)(OH)_{12} \cdot 4H_2O + 12H^+$	-74.00
CaMoO ₄ precipitation	$Ca^{2+} + MoO_4^{2-} \Leftrightarrow CaMoO_{4(s)}$	7.90

^c For edge sorption on AFm-SO₄.

Table S6. Physical parameters of AFm particles.

AFm-Cl ₂	$\frac{SA^{1}}{(m^{2} g^{-1})}$ 3.5	AEL ² (μm) 0.5	Density (g cm ⁻³) 2.11	Basal area (m^2) 6.50×10^{-13}	LEP ³ (nm g ⁻¹) 2.23×10^{17}	$\frac{\text{LS}^4}{(\text{nm}^2 \text{ g}^{-1})}$ 2.19×10 ¹⁸
AFm-SO ₄	1.9	5.0	2.02	6.50×10 ⁻¹¹	2.26×10 ¹⁶	2.29×10 ¹⁷

 ¹ SA represents specific surface area measured by N₂-sorption BET.
 ² AEL represents average edge length of AFm particles measured by SEM.
 ³ LEP represents lateral edge perimeter.
 ⁴ LS represents lateral surface. 223

225 **Table S7.** Edge sites concentration and adsorbed anion amount.

	LEP length conc. (nm L ⁻¹)	LS area conc. $(nm^2 L^{-1})$	LEP site conc. (mol L ⁻¹)	LS site conc. (mol L ⁻¹)	Sample	Adsorbed Mo amount (mol L ⁻¹)
AFm-Cl ₂	4.45×10 ¹⁷	4.38×10 ¹⁸	7.39×10 ⁻⁷	1.94×10 ⁻⁵	ClA ClB	7.86×10 ⁻⁷ 4.94×10 ⁻⁶
-					ClC	1.98×10 ⁻⁵
					SA	5.25×10 ⁻⁸
AFm-SO ₄	3.52×10 ¹⁶	3.57×10 ¹⁷	5.85×10 ⁻⁸	1.58×10 ⁻⁶	SB	2.78×10 ⁻⁷
					SC	1.63×10 ⁻⁶

* The L/S ratio of 500 kg/kg was used. Layers' edge and lateral adsorption site densities are estimated as 1.00 nm⁻¹ and 2.67 nm⁻² (2.67 Ca atoms are included per area of 8.700×11.517 Å², seeing Figure S13), respectively. LS and LEP represent lateral surface and lateral edge perimeter, respectively.

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