

Supplementary information

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S1. DLVO calculations

The DLVO model calculations are performed using the approach published by Mahmood et al. [1]. This approach calculates the interaction force between clay colloids. In this study, the authors used the approach of Mahmood et al. [1] to calculate the total interaction energy as sum of the interactions between edge-edge (EE), edge-face (EF) and face-face (FF). Therefore, the given formulas are reconverted to yield the interaction energy.

S1.1. Calculation of FF (face-face) interaction

The hydration energy is calculated using the equation given by [2]:

$$V_H^{FF} = KhA_F \cdot \exp\left(-z/h\right) \quad (S1)$$

where K is the hydration force constant, h is the decay length, A_F is the face surface area of the colloid and z is the separation distance. The Born repulsion can be calculated as [1]:

$$V_B^{FF} = \frac{A_H A_F \sigma^6}{360\pi z^8} \quad (S2)$$

where A_H is the Hamaker constant and σ is the collision diameter, usually estimated to be 0.5 nm. The electric double layer interaction energy between two flat platelets with the same surface ζ -potential ($\varphi_i = \varphi_f$) can be calculated using the linear superposition approximation (LSA) from Gregory [3]

$$V_{EDL}^{FF} = \frac{64nA_F k_B T}{\kappa} \tanh^2\left(\frac{e v \varphi_f}{4k_B T}\right) \cdot \exp(-\kappa z) \quad (S3)$$

where k_B is the Boltzmann constant, T the absolute temperature, e the elementary charge and v the valence of the ion. The number concentration n_i of an ion i can be calculated from its concentration c_i with the Avogadro constant N_A .

$$n_i = 1000 \cdot N_A \cdot c_i = 6.022 \cdot 10^{26} \cdot c_i \quad (S4)$$

The reciprocal double layer thickness κ can be expressed as:

$$\kappa^2 = 1000N_A \sum_i c_i v_i^2 \frac{e^2}{\varepsilon_r \varepsilon_0 k_B T} \quad (S5)$$

where ε_r is the relative permittivity of water and ε_0 the dielectric permittivity of vacuum. The London-van der Waals attraction energy can be calculated by the equation derived by Verwey and Overbeek [4]:

$$V_{VDW}^{FF} = \frac{A_H A_F}{12\pi z^2} \quad (S6)$$

S1.2 Calculation of EF (edge-face) interaction

The hydration interaction energy between a flat face and a half cylinder is calculated using the expression [1]:

$$V_H^{EF} = Khl\sqrt{2\pi hr} \cdot \exp\left(-z/h\right) \quad (S7)$$

The Born repulsion is calculated by

$$V_B^{EF} = \frac{A_H \sigma^6 l r}{180\pi} \sum_{n=0}^N \frac{\Delta\theta}{[z + r - r \cos(n\Delta\theta)]^8} \quad (S8)$$

where l is the length of the half cylinder, r the radius of the half cylinder and θ the angle between individual stripes of the half cylinder surface. A value for N = 550 is used in accordance with Mahmood et al. [1]. With this value, the result is found to converge within 5 % of the final value. The electronic double layer interaction term is calculated using:

$$V_{EDL}^{EF} = \frac{64nk_B T l}{\kappa} \sqrt{\frac{2\pi r}{\kappa}} \tanh\left(\frac{ev\phi_f}{4k_B T}\right) \tanh\left(\frac{ev\phi_e}{4k_B T}\right) \exp(-\kappa z) \quad (S9)$$

where ϕ_e is the edge ζ -potential recalculated from the ζ -potentials of alumina and silica as proposed by Williams and Williams [5]. The van der Waals interaction energy is calculated using the expression:

$$V_{VDW}^{EF} = -\frac{A_H l \sqrt{r}}{12\sqrt{2} z^{3/2}} \quad (S10)$$

S1.3 Calculation of EE (edge-edge) interaction

The hydration interaction energy is calculated using the expression derived from Mahmood et al. [1]:

$$V_H^{EE} = K h l \sqrt{\pi h r} \cdot \exp\left(-z/h\right) \quad (S11)$$

The Born repulsion interaction energy between two edges is obtained using:

$$V_B^{EE} = \frac{A_H \sigma^6 l r}{180\pi} \sum_{n=0}^N \frac{\Delta\theta}{[z + 2r - 2r \cos(n\Delta\theta)]^8} \quad (S12)$$

where a value of 550 is used again for N. The electronic double layer interaction energy is calculated by:

$$V_{EDL}^{EE} = \frac{64nk_B T l}{\kappa} \sqrt{\frac{\pi r}{\kappa}} \tanh^2\left(\frac{ev\phi_e}{4k_B T}\right) \exp(-\kappa z) \quad (S13)$$

and the van der Waals interaction energy as:

$$V_{VDW}^{EE} = -\frac{A_H l \sqrt{r}}{24 z^{3/2}} \quad (S14)$$

Figures

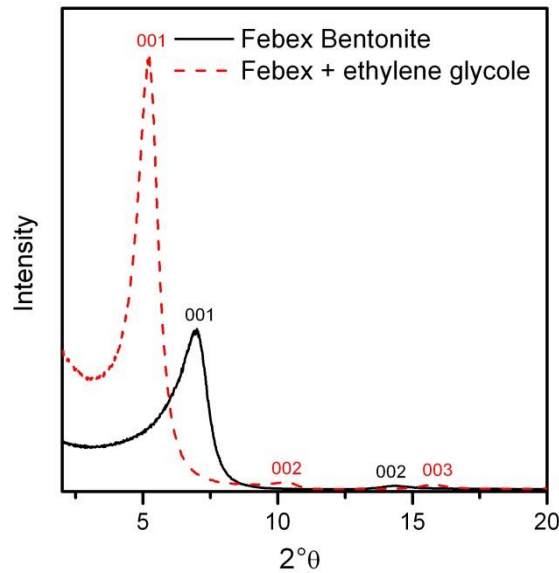


Figure S1. XRD diffractogram of the bentonite colloids used throughout this study.

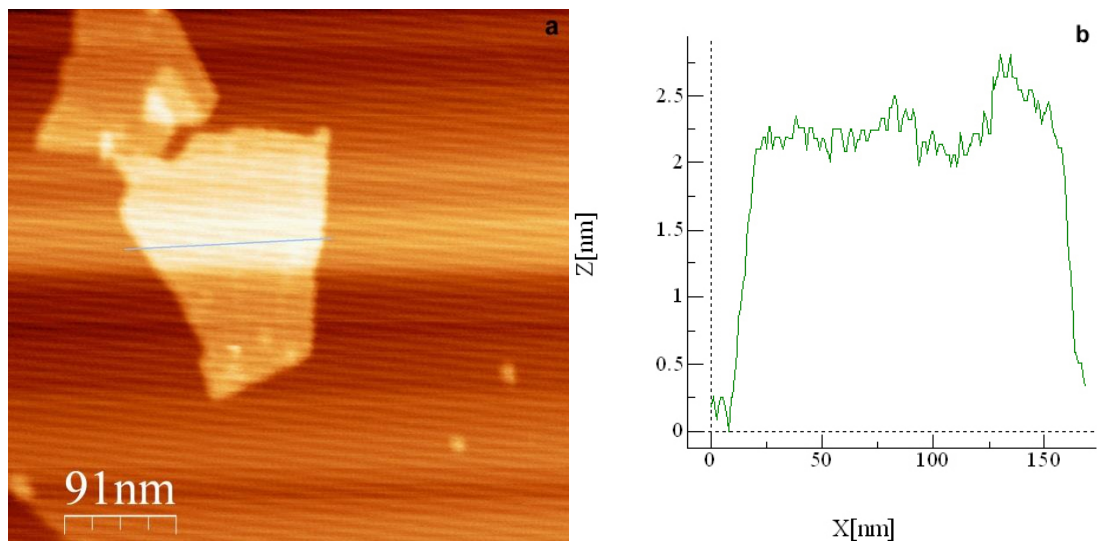


Figure S2. (a) AFM image of a representative Febex bentonite colloid deposited onto a mica. (b) line profile over the Febex bentonite colloid indicated by the line in (a). The line profile is not corrected for tip artifacts. The total number of samples $n = 10$.

Tables

Table S1. List of values used for the calculations.

Description	Input Parameter	Reference
K (N m ⁻²)	1.6·10 ⁶	[1]
h (m)	0.9 10 ⁻⁹	[1]
A _H (J)	2.72 10 ⁻²⁰	[6]
σ (m)	0.5 10 ⁻⁹	[1]
l (m)	1.4 10 ⁻⁷	this study
r (m)	1 10 ⁻⁹	this study
A (m ²)	1.92 10 ⁻¹⁴	this study
ε ₀ (C V ⁻¹ m ⁻¹)	8.854187817 10 ⁻¹²	
ε _r ()	78.25	
k _B (J K ⁻¹)	1.3806504 10 ⁻²³	
e (C)	1.602176487 10 ⁻¹⁹	
Δθ ()	0.002855933	
N _A (mol ⁻¹)	6.022 141 79 10 ²³	
T (K)	298.15	

Table S2. Linear fit ζ-potential of the measured ζ-potential of Febex bentonite colloids in NaCl and CaCl₂ background electrolyte solution.

Electrolyte	Concentration (mmol L ⁻¹)	ζ-potential at pH (mV)				
		6	7	8	9	10
NaCl	1			-28.5		
	100			-29		
CaCl ₂	33.0	-2.7	-4.3	-5.9	-7.5	-9.1
	0.33	-16.3	-17.9	-19.5	-21.1	-22.7

Table S3. Used ζ -potential of silica (Aerosil90, Degussa) for the DLVO calculations in NaCl and CaCl₂ background electrolyte solution.

Electrolyte	Concentration (mmol L ⁻¹)	ζ -potential at pH (mV)				
		6	7	8	9	10
NaCl	1	-7.7	-9.5	-11.3	-13.1	-14.9
	100	-18.1	-23.2	-28.3	-33.4	-38.5
CaCl ₂	33.0	-1.8	-3.2	-4.6	-6.1	-7.5
	0.33	-20	-21.9	-23.8	-25.7	-27.6

Table S4. ζ -potential of alumina phases used in the DLVO calculations in NaCl and CaCl₂ background electrolyte solution.

Phase	Electrolyte	Concentration (mmol L ⁻¹)	ζ -potential at pH (mV)					Source
			6	7	8	9	10	
α -alumina	NaCl	1	26.4	25.5	20.2	8.9	-5.2	this study
		100	47.1	43.2	34.3	19.0	-2.8	
α -alumina	CaCl ₂	33.0	32.7	28.0	23.3	18.6	13.9	this study
		0.33	43.0	38.9	32.4	23.5	12.2	
γ -alumina	NaCl	1	20.5	8.3	-3.3	-10.4	-9.1	[7]
		100	42.6	29.7	11.9	-8.0	-27.3	
α -alumina _{Kup}	NaCl	1	16.2	10.5	4.7	-0.9	-6.1	[8]
		100	36.8	28.0	13.5	-3.6	-17.4	

Table S5. Estimated edge electrokinetic ζ -potential for the DLVO calculations in NaCl and CaCl₂ background electrolyte solution.

Alumina Phase	Silica/Alumina-Ratio	Electrolyte	Concentration (mmol L ⁻¹)	ζ -potential at pH (mV)				
				6	7	8	9	10
α -Al ₂ O ₃	72 % / 28 %	NaCl	1	1.8	0.3	-2.5	-6.9	-12.2
			100	0.2	-4.6	-10.8	-18.7	-28.5
α -Al ₂ O ₃	72 % / 28 %	CaCl ₂	33.0	7.9	5.5	3.2	0.8	-1.5
			0.33	-2.4	-4.9	-8.1	-11.9	-16.5
α -Al ₂ O ₃	87.4 % / 12.6 %	NaCl	1	-3.4	-5.1	-7.3	-10.3	-13.7
			100	-9.9	-14.8	-20.4	-26.8	-34.0
γ -Al ₂ O ₃	72 % / 28 %	NaCl	1	0.2	-4.5	-9.1	-12.3	-13.3
			100	-1.1	-8.4	-17.0	-26.3	-35.4
α -Al ₂ O ₃	72 % / 28 %	NaCl	1	-1.0	-3.9	-6.8	-9.7	-12.4
			100	-2.7	-8.9	-16.6	-25.0	-32.6

Table S6. Used face surface electrokinetic ζ -potential (best fit) after fitting the W_{DLVO} values to the $W_{measured}$ values in NaCl and CaCl₂ background electrolyte solution. The surface electrokinetic potentials in NaCl background electrolyte solution are the average values of all used alumina phases. The CaCl₂ background electrolyte solution is solely calculated with α -alumina.

Electrolyte	Concentration (mmol L ⁻¹)	ζ -potential at pH (mV)				
		6	7	8	9	10
NaCl	1	-31.7	-31.6	-31	-30	-28.7
	100	-12.6	-18.9	-25.4	-29.9	-33.7
CaCl ₂	33.0	-1.8	-3.2	-4.6	-6.1	-7.5
	0.33	-16	-19.9	-23.6	-22.7	-20.5

Table S7. Fitted theoretical CCC concentrations to match the CCC criteria of $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$ and $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$ using the DLVO approach with constant surface potential and estimated edge electrokinetic potential (α -alumina).

Conc. (mmol·L ⁻¹)	pH	Na-CCC (mmol·L ⁻¹)	Surface Potential	Conc. (mmol·L ⁻¹) at $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$				Conc. (mmol·L ⁻¹) at $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$			
				total	ff	ef	ee	total	ff	ef	ee
1	6	15	ζ -potential ⁽¹⁾	620	685	n. b. ⁽²⁾	n. b.	593	652	n. b.	n. b.
	7	20		623	685	n. b.	n. b.	596	652	n. b.	n. b.
	8	200		628	685	84	n. b.	601	652	n. b.	n. b.
	9	250		635	685	229	106	608	652	92	n. b.
	10	350		646	685	389	379	620	652	229	177
	6	15	best fit ⁽³⁾	718	783	n. b.	n. b.	692	751	n. b.	n. b.
	7	20		717	779	n. b.	n. b.	692	748	n. b.	n. b.
	8	200		703	761	101	n. b.	678	729	n. b.	n. b.
	9	250		680	730	245	106	654	698	105	n. b.
	10	350		651	690	391	379	624	657	231	177
100	6	15	ζ -potential	635	700	n. b.	n. b.	608	667	n. b.	n. b.
	7	20		635	700	n. b.	n. b.	608	668	n. b.	n. b.
	8	200		637	700	n. b.	n. b.	610	668	n. b.	n. b.
	9	250		640	700	n. b.	n. b.	613	668	n. b.	n. b.
	10	350		644	700	114	n. b.	618	668	n. b.	n. b.
	6	15	best fit	5	2	n. b.	n. b.	9	4	n. b.	n. b.
	7	20		312	373	n. b.	n. b.	284	337	n. b.	n. b.
	8	200		526	588	n. b.	n. b.	498	554	n. b.	n. b.
	9	250		669	729	n. b.	n. b.	642	696	n. b.	n. b.
	10	350		n. b.	n. b.	645	n. b.	n. b.	n. b.	471	n. b.

(1) ζ -potential = measured Febex bentonite ζ -potential, (2) n. b. = no energy barrier, (3) best fit = best fit surface potential.

Table S8. Fitted theoretical CCC concentrations to match the CCC criteria of $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$ and $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$ using the DLVO approach with constant surface potential and estimated edge electrokinetic potential (α -alumina taken from Kupcik et al. [8]).

Conc. (mmol·L ⁻¹)	pH	Na-CCC (mmol·L ⁻¹)	Surface Potential	Conc. (mmol·L ⁻¹) at $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$				Conc. (mmol·L ⁻¹) at $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$			
				total	ff	ef	ee	total	ff	ef	ee
1	6	15	ζ -potential ⁽¹⁾	622	685	n. b.	n. b.	595	652	n. b.	n. b.
	7	20		626	685	48	n. b.	599	652	13	n. b.
	8	200		633	685	192	58	606	652	62	n. b.
	9	250		642	685	334	275	615	652	180	93
	10	350		651	685	451	509	625	652	285	292
	6	15	best fit ⁽³⁾	720	783	n. b.	n. b.	694	751	n. b.	n. b.
	7	20		720	779	65	n. b.	695	748	n. b.	n. b.
	8	200		709	761	216	58	683	729	82	n. b.
	9	250		687	730	354	275	661	698	168	93
	10	350		656	690	453	509	630	657	287	292
100	6	15	ζ -potential	636	700	n. b.	n. b.	609	667	n. b.	n. b.
	7	20		638	700	n. b.	n. b.	611	667	n. b.	n. b.
	8	200		640	700	n. b.	n. b.	613	667	n. b.	n. b.
	9	250		642	700	66	n. b.	615	667	n. b.	n. b.
	10	350		645	700	118	n. b.	618	667	n. b.	n. b.
	6	15	best fit	5	2	n. b.	n. b.	8	4	n. b.	n. b.
	7	20		315	373	n. b.	n. b.	287	337	n. b.	n. b.
	8	200		529	588	n. b.	n. b.	5601	554	n. b.	n. b.
	9	250		671	729	72	n. b.	644	696	n. b.	n. b.
	10	350		786	842	154	n. b.	761	812	n. b.	n. b.

(1) ζ -potential = measured Febex bentonite ζ -potential, (2) n. b. = no energy barrier, (3) best fit = best fit surface potential.

Table S9. Fitted theoretical CCC concentrations to match the CCC criteria of $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$ and $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$ using the DLVO approach with constant surface potential and estimated edge electrokinetic potential (γ -alumina taken from de Lint et al. [7]).

Conc. (mmol·L ⁻¹)	pH	Na-CCC (mmol·L ⁻¹)	Surface Potential	Conc. (mmol·L ⁻¹) at $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$				Conc. (mmol·L ⁻¹) at $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$			
				total	ff	ef	ee	total	ff	ef	ee
1	6	15	ζ -potential ⁽¹⁾	621	685	n. b.	n. b.	594	652	n. b.	n. b.
	7	20		626	685	n. b.	n. b.	599	652	n. b.	n. b.
	8	200		634	685	199	67	607	652	68	n. b.
	9	250		644	685	355	313	617	652	198	123
	10	350		655	685	491	601	628	652	322	278
	6	15	best fit ⁽³⁾	719	783	n. b.	n. b.	693	751	n. b.	n. b.
	7	20		720	779	55	n. b.	694	748	n. b.	n. b.
	8	200		709	761	224	67	683	729	88	n. b.
	9	250		688	730	376	313	662	698	217	123
	10	350		659	690	494	601	633	657	325	378
100	6	15	ζ -potential	636	700	n. b.	n. b.	609	667	n. b.	n. b.
	7	20		638	700	n. b.	n. b.	611	667	n. b.	n. b.
	8	200		642	700	54	n. b.	615	667	n. b.	n. b.
	9	250		644	700	116	n. b.	618	667	n. b.	n. b.
	10	350		645	700	135	n. b.	619	667	n. b.	n. b.
	6	15	best fit	5	2	n. b.	n. b.	9	4	n. b.	n. b.
	7	20		315	373	n. b.	n. b.	288	337	n. b.	n. b.
	8	200		531	588	n. b.	n. b.	503	554	n. b.	n. b.
	9	250		673	729	124	n. b.	647	696	n. b.	n. b.
	10	350		787	842	174	n. b.	762	812	n. b.	n. b.

(1) ζ -potential = measured Febex bentonite ζ -potential, (2) n. b. = no energy barrier, (3) best fit = best fit surface potential.

Table S10. Fitted theoretical CCC concentrations to match the CCC criteria of $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$ and $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$ using the DLVO approach with constant surface potential and estimated edge electrokinetic potential for 5 % structural Al-ratio (α -alumina).

Conc. (mmol·L ⁻¹)	pH	Na-CCC (mmol·L ⁻¹)	Surface Potential	Conc. (mmol·L ⁻¹) at $V_{\max} \leq 1 \text{ Jk}_B^{-1}\text{T}^{-1}$				Conc. (mmol·L ⁻¹) at $V_{\max} \leq 10 \text{ Jk}_B^{-1}\text{T}^{-1}$			
				total	ff	ef	ee	total	ff	ef	ee
1	6	15	ζ -potential ⁽¹⁾	627	685	67	n. b.	600	652	n. b.	n. b.
	7	20		631	685	159	n. b.	605	652	13	n. b.
	8	200		637	685	258	149	610	652	116	n. b.
	9	250		644	685	363	328	618	652	205	135
	10	350		653	685	471	555	626	652	304	334
	6	15	best fit ⁽³⁾	725	783	87	n. b.	699	751	n. b.	n. b.
	7	20		725	779	187	n. b.	700	748	1	n. b.
	8	200		712	761	287	149	687	729	140	n. b.
	9	250		689	730	384	328	663	698	224	135
	10	350		658	690	474	555	631	657	306	334
100	6	15	ζ -potential	638	700	n. b.	n. b.	611	667	n. b.	n. b.
	7	20		639	700	n. b.	n. b.	612	667	n. b.	n. b.
	8	200		640	700	n. b.	n. b.	614	667	n. b.	n. b.
	9	250		643	700	78	n. b.	616	667	n. b.	n. b.
	10	350		646	700	143	n. b.	619	667	n. b.	n. b.
	6	15	best fit	4	2	n. b.	n. b.	7	4	n. b.	n. b.
	7	20		316	373	n. b.	n. b.	288	337	n. b.	n. b.
	8	200		529	588	n. b.	n. b.	501	554	n. b.	n. b.
	9	250		671	729	84	n. b.	645	696	n. b.	n. b.
	10	350		787	842	182	n. b.	763	812	1	n. b.

(1) ζ -potential = measured Febex bentonite ζ -potential, (2) n. b. = no energy barrier, (3) best fit = best fit surface potential.

List of symbols

Symbol	Entity	Name
V	J	Interaction energy
K	N m^{-2}	Hydration force constant
h	m	Decay length
z	m	Separation distance
A_H	J	Hamaker constant
σ	m	Collision diameter
ϵ_0	$\text{C V}^{-1} \text{m}^{-1}$	Dielectric permittivity of vacuum
ϵ_r		Relative permittivity of water at 25 °C
κ	m^{-1}	Reciprocal double layer thickness
k_B	J K^{-1}	Boltzmann constant
e	C	Elementary charge
c	mol L^{-1}	Bulk concentration of electrolyte
v		Valence of ion
φ_f	V	Face ζ -potential
φ_e	V	Edge ζ -potential
l	m	Colloid edge length
r	m	Colloid edge radius
A_F	m^2	Surface area of colloid face
θ		Angle between individual strips of half cylinder
T	K	Absolute temperature
N_A	mol^{-1}	Avogadro constant

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