IRREVERSIBILITY OF BENTONITE COLLOID AGGREGATION UNDER DIFFERENT ENVIRONMENTS

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Motivation

Bentonite colloid STABILITY is a necessary condition for bentonite erodibility and for colloid mobility.

- Stability studies analyse whether colloids aggregate as function of several chemical and physical parameters:

  **pH, ionic strength, temperature and presence of multivalent ions, or organic ligands, have been widely analysed.*

Motivation

- Repository scenarios with high saline groundwater (GW) expect negligible colloid concentration.

- In the time frame of repositories, GW conditions may evolve.

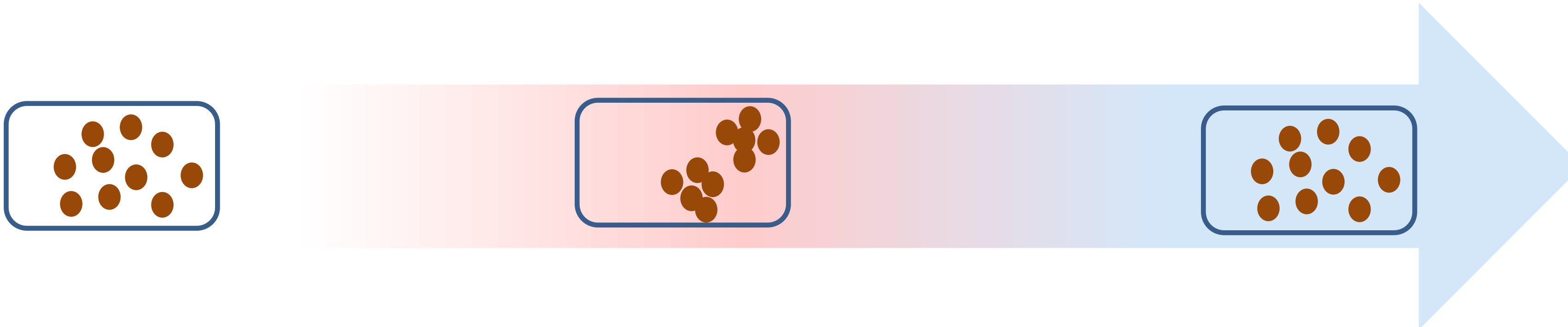
Recharge water (i.e. rivers, lakes, rain or water from melting ice sheet) may **reduce groundwater salinity.**

- Disaggregation processes have been scarcely investigated.

Bentonite colloid DISAGGREGATION?

Aim

To study the (ir)reversibility of clay colloid aggregation



STABLE BC | **AGGREGATION** | **DISAGGREGATION**

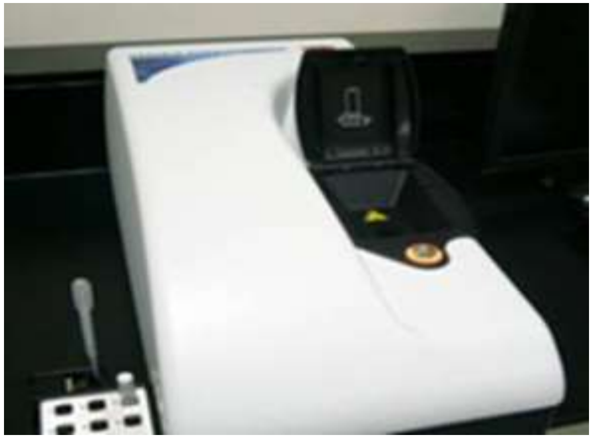
<u>**Ionic strength increase / decrease**</u>

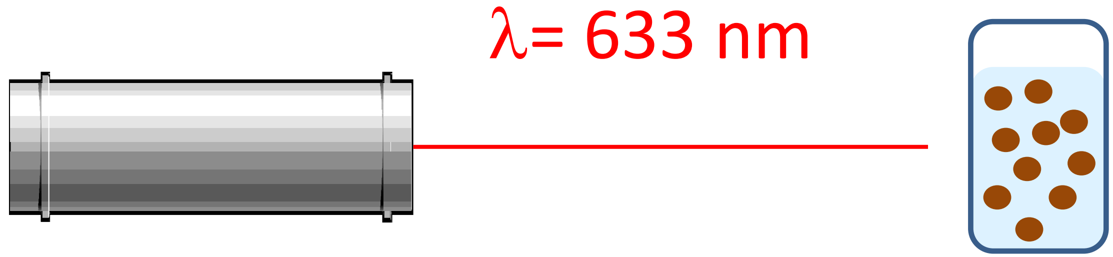
Different methods & experimental times

Summary of experiments

	Experiment	Output	Method
(I)	Aggregation kinetics (Na, Ca)	Diameter evolution (60 min)	TR-PCS
	Ionic strength (I) increase	***Attachment coefficients*	
(II)	Progressive disaggregation	Diameter progressive decrease	PCS
	I decrease- Dialysis	Diameter evolution (60 days)	
(III)	Disaggregation kinetics	Diameter evolution (60 min)	TR-PCS
	I decrease- dilution	***Detachment coefficients*	
		Size distribution - *stable fraction*	SPC
(IV)	Aggregation history ($NaClO_4$, Na-Ca, $CaCl_2$)	Diameter increase	PCS
	Disaggregation in different GW	Diameter decrease	

Photon Correlation Spectrometry (PCS) technique





- Time dependent fluctuations of scattering light intensity

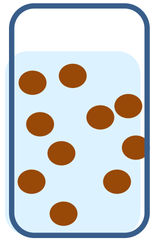
- Time-resolved dynamic light experiments:
- Kinetics of colloid (dis)aggregation (1 hour)

Average hydrodynamic diameter
Evolution

(I) Aggregation experiments: Experimental

INITIAL –Bentonite Colloids

- **Na-FEBEX** bentonite colloids.
- $NaClO_4$ 0.5 mM.

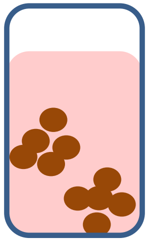


pH 6.5 ± 0.5.

Average diameter (PCS): 300 nm

Stable - REFERENCE

AGGREGATION

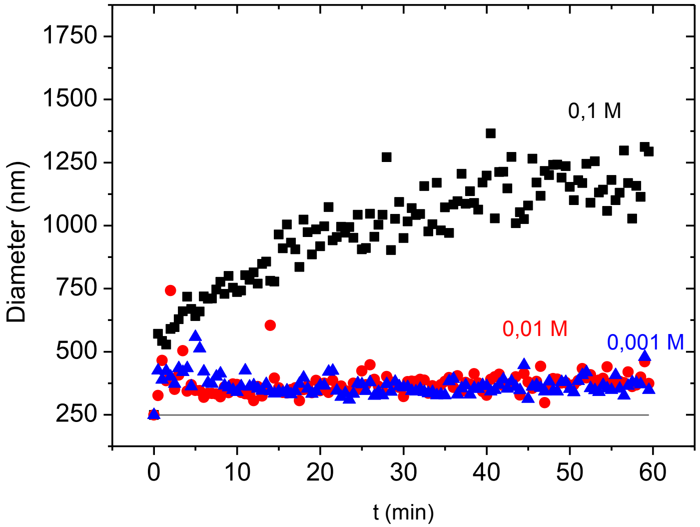


- Induced by ionic strength increase:
- Different electrolytes

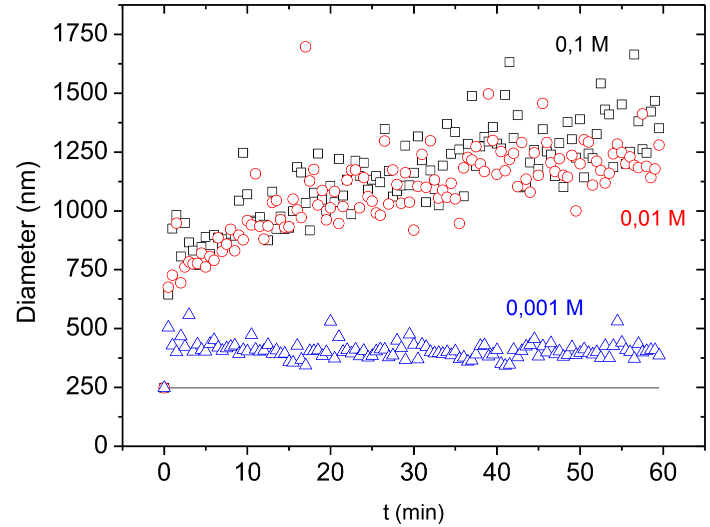
$NaClO_4$ | **Na - Ca mixed** | **$CaCl_2$**

(I) Aggregation experiments: Results

$NaClO_4$



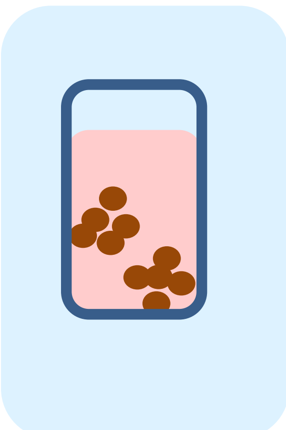
Na - Ca mixed



- ✓ Increasing ionic strength, bentonite colloid aggregation is fast.
- ✓ Bivalent ions favour aggregation (lower CCC), as Schulze-Hardly rule predicts.

(II) Disaggregation experiments: Dialysis

Aggregation in 0.1 M $NaClO_4$



(A) Progressive ionic strength decrease (no dilution)

- $1 \cdot 10^{-2}$ M
- $1 \cdot 10^{-3}$ M
- $5 \cdot 10^{-4}$ M

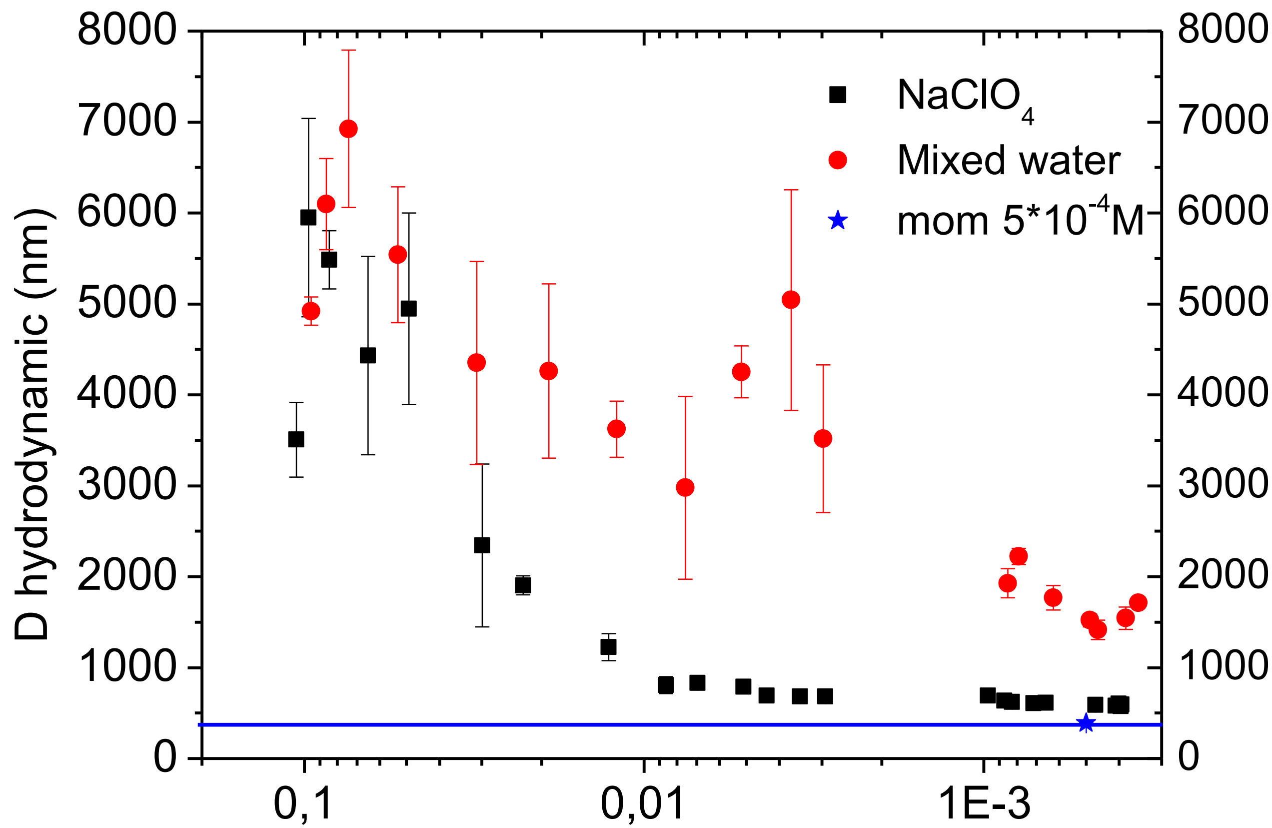
$CaCl_2$

Na - Ca mixed electrolyte

$NaClO_4$

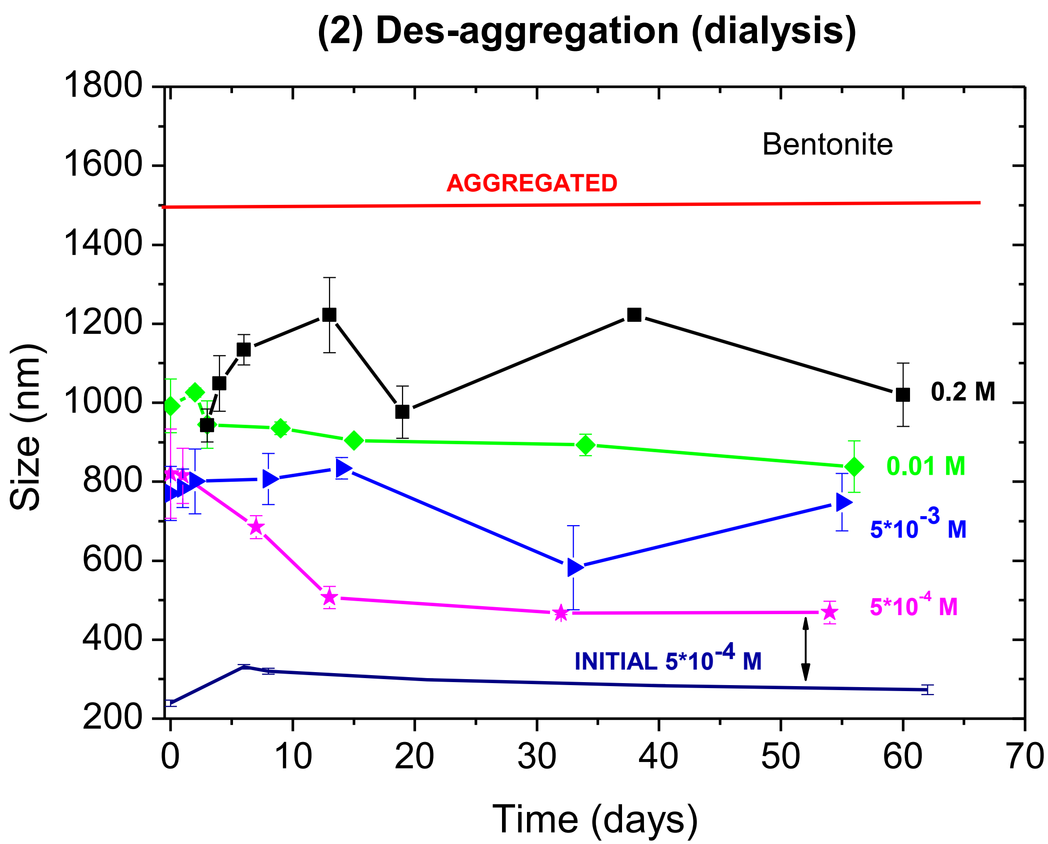
(B) Temporal evolution (60 days)

(II) Disaggregation experiments: Dialysis



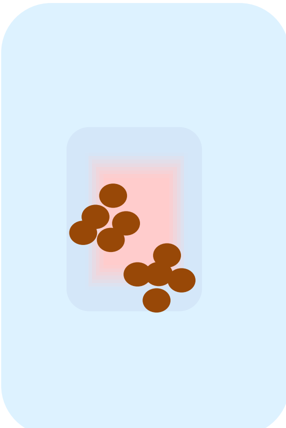
- ✓ By decreasing ionic strength bentonite particles are disaggregated, but not completely.
- ✓ Disaggregation is less effective in presence of Ca.

(II) Disaggregation experiments: Temporal evolution



- ✓ Average particle diameter in disaggregated decreases at lower ionic strength .
- ✓ Initial stable size (300 nm) is not recovered.

(III) Disaggregation kinetics by dilution



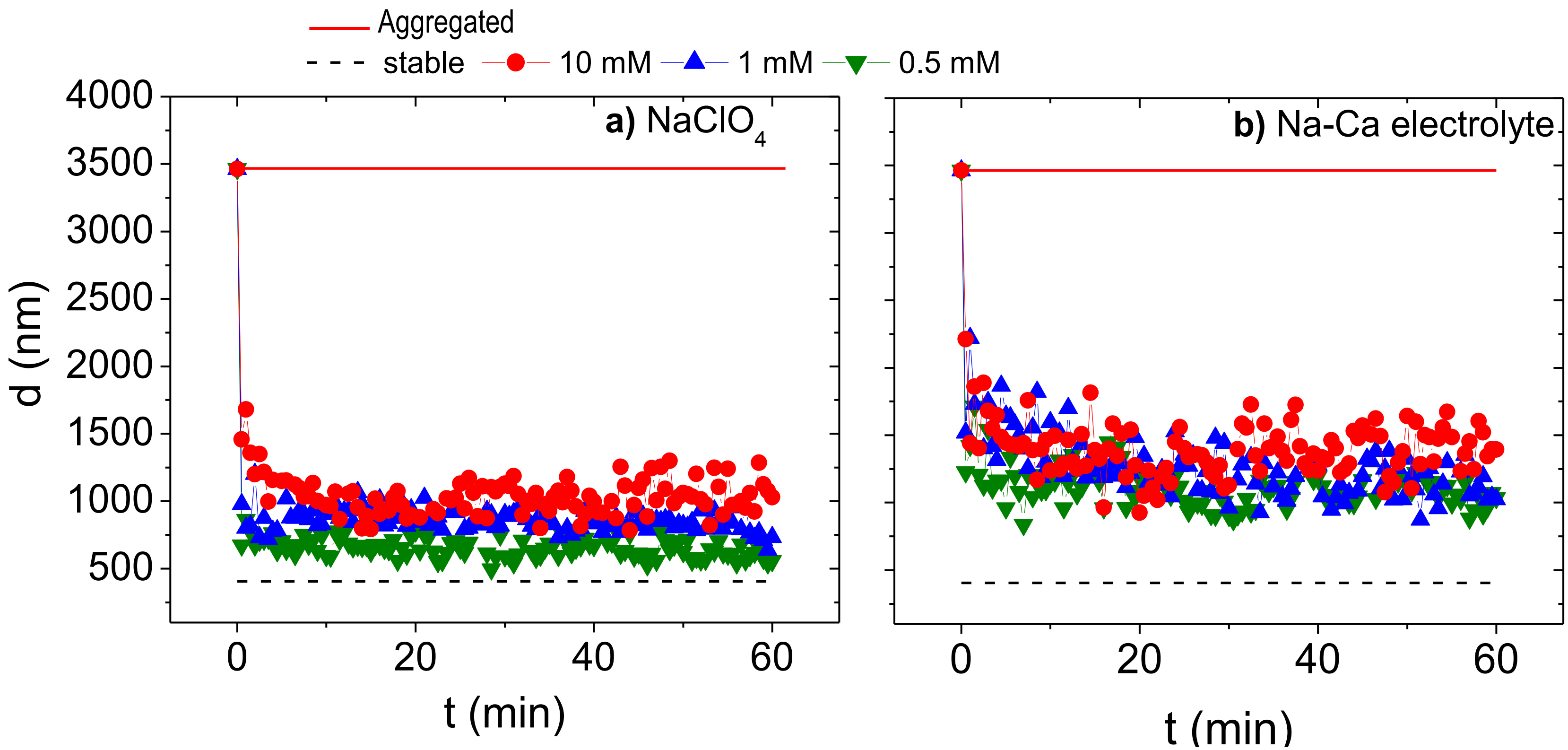
Aggregation 0.1 M 500 ppm

IONIC STRENGHT DECREASE + DILUTION
in the same electrolyte

--$1\cdot10^{-2}$ M; --$1\cdot10^{-3}$ M; --$5\cdot10^{-4}$ M

CaCl2 | **Na - Ca mixed** | **$NaClO_4$**

(III) Disaggregation kinetics by dilution



- ✓ By decreasing ionic strength, bentonite colloid disaggregation is promoted, more efficiently in absence of Ca.
- ✓ Initial size (300 nm) is not recovered.

(III) Fast disaggregation experiments by dilution

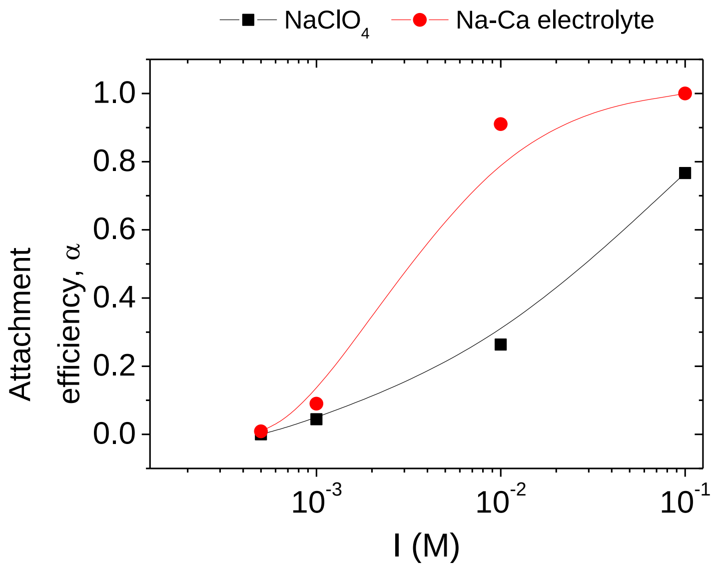
Attachment

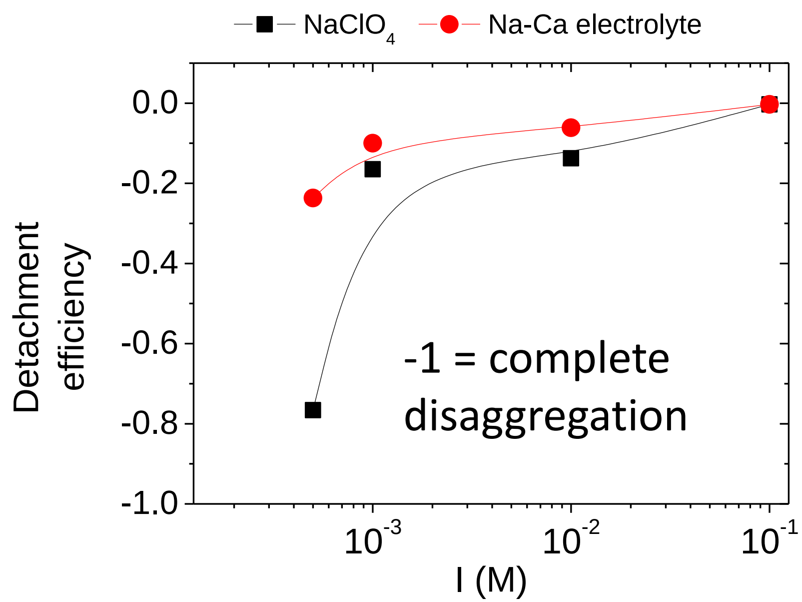
$$\alpha = \frac{1}{W} = \frac{\left(\frac{\delta d_h}{\delta t}\right)_{t\to 0}}{\left(\frac{\delta d_h}{\delta t}\right)_{fast}}$$

0 = stable
1 = fast regime
DL suppressed

Detachment

$$Det. = -\frac{\left(\frac{\delta d_h}{\delta t}\right)_{t\to 0}}{\left(\frac{\delta d_h}{\delta t}\right)_{fast}}$$





✓ Hysteresis, different kinetics: Irreversible process

(III) Fast disaggregation experiments by dilution: SPC

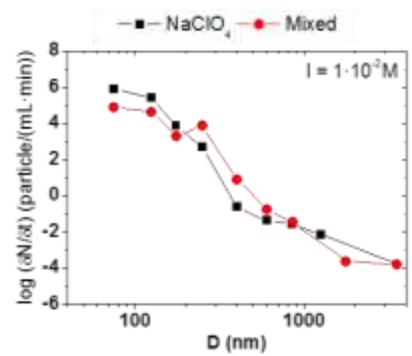
Single Particle Counter (SPC)

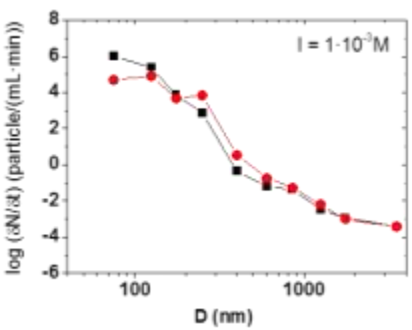
- Particle population within different size channels.
- Particle concentration normalized to size interval.

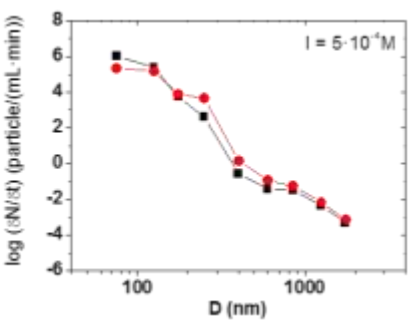
$$\frac{\delta N}{\delta d} = \frac{[particle\ concentration]}{(d_{upper}-d_{lower})_{channel\ i}}$$

- Disaggregated samples where not shaken to determine the size distribution of -only- **stable fraction of colloids.**

(III) Fast disaggregation experiments by dilution: SPC







- $NaClO_4$: >99% BC in channels (50-150) nm
- Na-Ca: >99% BC in channels (50-300) nm

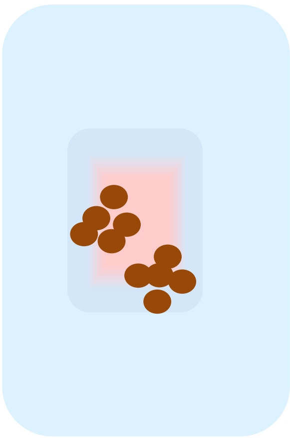
Particle % corresponding to each size channel

Channel (nm)	*Cl 1·10⁻²M*	*Cl 1·10⁻³M*	*Cl 5·10⁻⁴M*	*M 1·10⁻²M*	*M 1·10⁻³M*	*M 5·10⁻⁴M*
50-100	76.27	79.96	80.82	56.03	33.65	56.08
100-150	22.97	19.35	18.65	31.69	53.79	39.54
150-200	0.67	0.58	0.46	1.41	3.29	2.01
200-300	0.09	0.11	0.07	10.85	9.27	2.37
300-500	9.00 E-05	1.30 E-04	8.00 E-04	0.024	0.0098	0.0015
500-700	1.52 E-05	2.00 E-05	1.16E-05	5.03 E-04	4.90 E-04	1.19 E-04
700-1000	1.50 E-05	2.01 E-05	1.58E-05	1.47 E-04	2.19 E-04	8.47 E-05
1000-1500	6.61 E-06	2.48 E-06	3.36 E-06	0.00 E+00	4.12 E-05	1.73 E-05
1500-2000	0.00 E+00	9.06 E-07	3.73 E-07	1.73 E-06	6.60 E-06	1.79 E-06
2000-5000	8.82 E-07	1.76 E-06	0.00 E+00	6.92 E-06	1.48 E-05	0.00 E+00

Ratio of concentration	
$NaClO_4$ $1·10^{-2}$M	0.82
$NaClO_4$ $1·10^{-3}$M	0.95
$NaClO_4$ $5·10^{-4}$M	0.97
Na-Ca water $1·10^{-2}$M	0.10
Na-Ca water $1·10^{-3}$M	0.11
Na-Ca water $5·10^{-4}$M	0.30

✓ Concentration of stable BC in disaggregated samples is lower than in the initial suspension.

(IV) Aggregation history



Aggregation 0.1 M 500 ppm

$CaCl_2$ **Na - Ca mixed** **$NaClO_4$**

--$1\cdot10^{-2}$ M; --$1\cdot10^{-3}$ M; --$5\cdot10^{-4}$ M

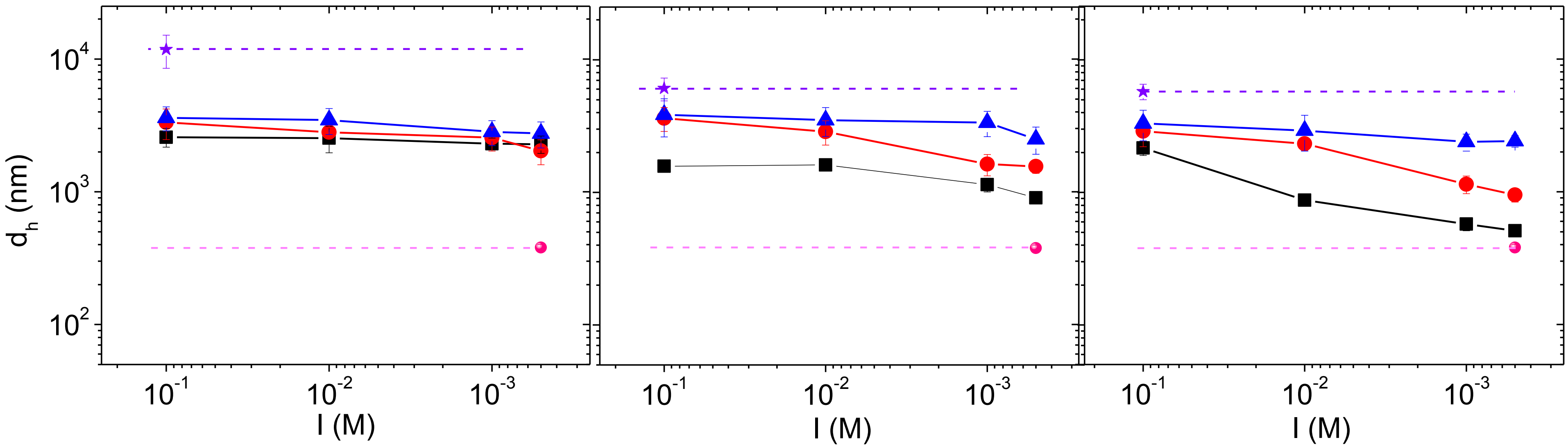
$CaCl_2$ **Na - Ca mixed** **$NaClO_4$**

Hydrodynamic diameter evolution

- Photon Correlation Spectrometry (PCS) measurements

(IV) Aggregation history

Aggregated in $CaCl_2$ | **Aggregated in Na - Ca** | **Aggregated in Na**



- ▲ Disaggregation in Ca^{2+}
- ● Disaggregation in Na^{+}-Ca^{2+}
- ■ Disaggregation in Na^{+}

✓ Particles aggregated in Ca waters are less effectively disaggregated.

Conclusions

- **Disaggregation of FEBEX bentonite colloids promoted by dilution to lower ionic strength was studied.**
- **Disaggregation was initially fast but, complete disaggregated state was not achieved, even at low ionic strength and in absence of divalent cations.**
- **In presence of Ca, the stable fraction of disaggregated colloids was low compared to the primary sample (< 10 %).**
- **The history of aggregation plays a role on further disaggregation.**
- **Overall results showed that the aggregation is not completely reversible, but disaggregation at longer times is not discarded.**

N. Mayordomo, C. Degueldre, U. Alonso, T. Missana. ***Size distribution of FEBEX bentonite colloids upon fast disaggregation in low ionic strength water (Clay Minerals, In press).***

Thank you for your attention!

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