BELBaR Project

The stability of clay colloids in groundwater

Summary for WP4

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ÚJV Řež, a. s., 2015

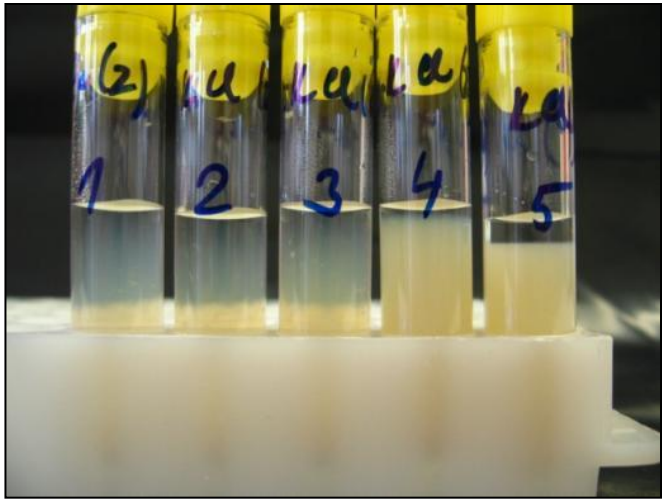
CP BELBAR WP4 MEETING
Karlsruhe - 12-13 October, 2015

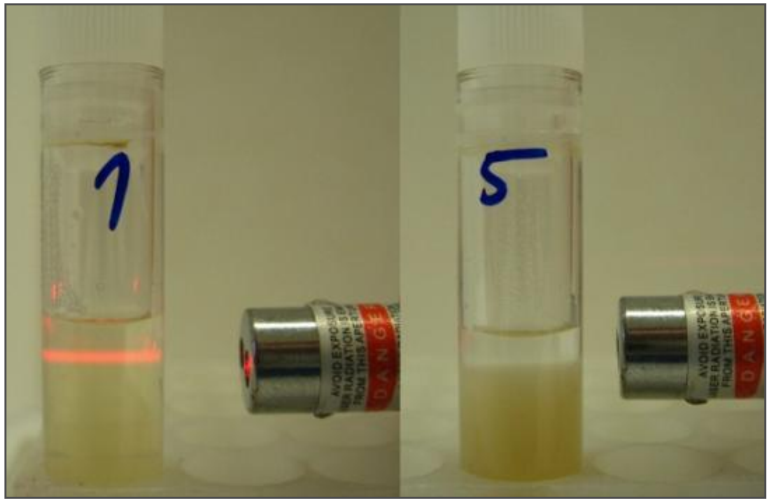
Issue: Colloid stability controlling processes

- Coagulation of clay dispersions by:
  - inorganic cations
  - effect of anions
  - effect of pH
  - effect of organic substances (humic acids)
  - coagulation kinetics

Issue: Colloid stability controlling processes - inorganic cations

- Series of test-tube tests
  - The C_C of univalent cations (Na^+, K^+) and divalent cations (Ca^{2+}, Mg^{2+}) were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (0.005 %, 0.05 % and 0.5 % w/w)
  - Electrolytes (NaCl, KCl, $CaCl_2$ and $MgCl_2$)
  - The final pH of solutions from 6.0 to 7.4
  - The visual inspection after 30 min. after the mixing, 24 hours after the re-mixing of the suspension and more than 48 hours and later with laser light beam[1)]. Colloids presence confirmed by photon cross correlation spectroscopy (PCCS)





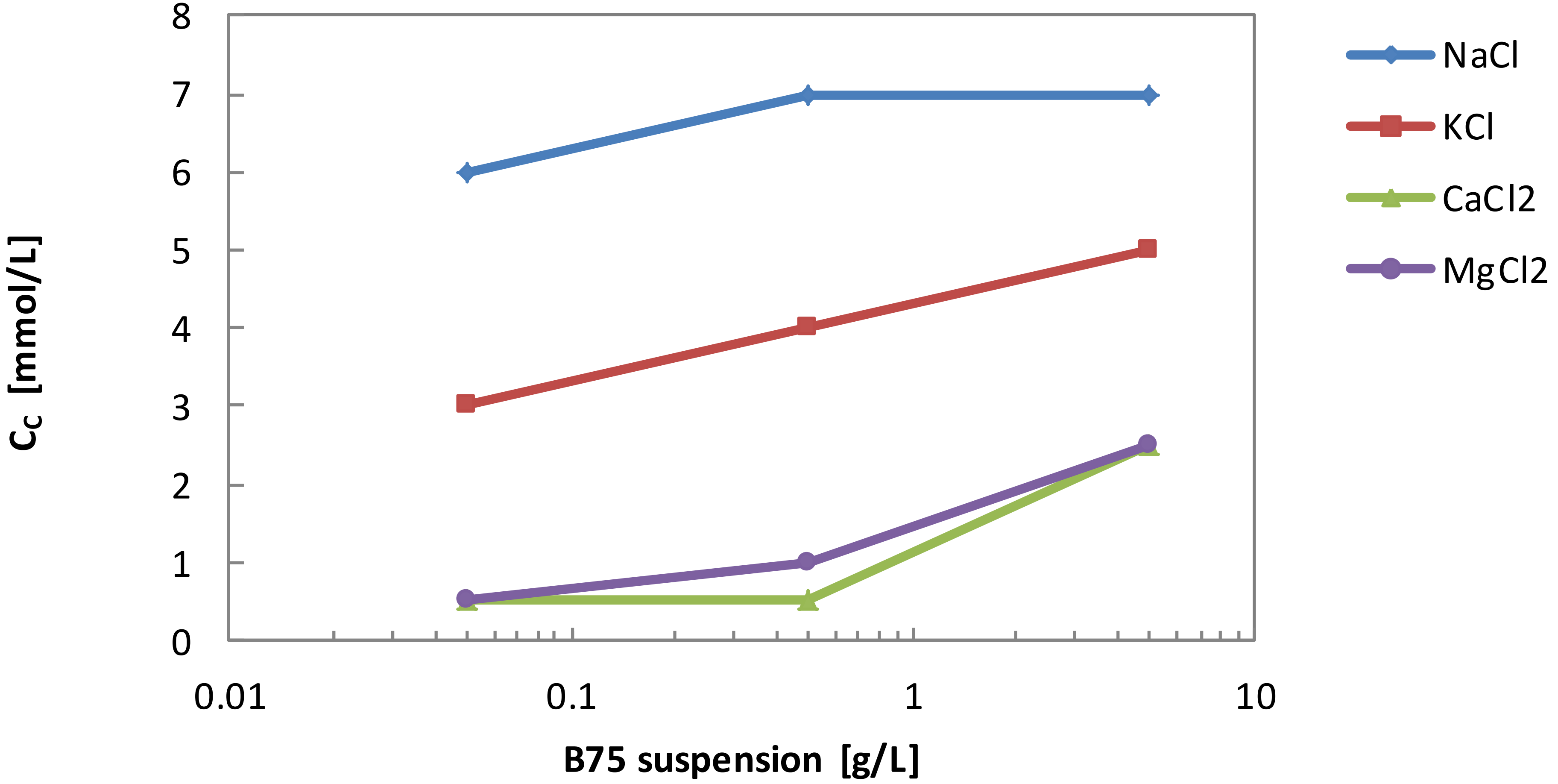
1} Berg J. C. (2010). An Introduction to Interfaces and Colloids: The Bridge to Nanoscience. World Scientific Publishing Co. Pte. Ltd., Singapore, 785 pp.

Issue: Colloid stability controlling processes - inorganic cations

- Does the cation exchange influence the C_C?
  - For dilute clay suspensions (up to 5g/l), the effect of cation exchange on C_C was not observed

	B75 Na+ 15/11/12	Clay susp. - pool of exchangeable cations			
	Cation occupancy	0.005 % w/w	0.05 % w/w	0.5 % w/w	
	meq/100g	50	500	5000	mg/l
Na+	33.97	0.0	0.2	1.7	mmol/l
K+	1.39	0.0	0.0	0.1	mmol/l
Mg2+	6.21	0.0	0.0	0.2	mmol/l
Ca2+	19.24	0.0	0.0	0.5	mmol/l

Issue: Colloid stability controlling processes - inorganic cations



Importance of divalent cations. The effect of increasing CCC with the solid content (concentration of bentonite in suspension).

Issue: Colloid stability controlling processes - inorganic cations (extended)

- Series of test-tube tests
  - The previous results were extended -> C_C of univalent cations (Li^+, Na^+, K^+, Rb^+, Cs^+) and divalent cations (Ca^{2+}, Mg^{2+}) were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (only for 50 mg/l)
  - Electrolytes (LiCl, NaCl, KCl, RbCl, CsCl and $CaCl_2$, $MgCl_2$)
  - The same visual and laser beam inspection, but the time was prolonged. Colloids presence confirmed more precisely by photon cross correlation spectroscopy (PCCS)

Salt	c_c (mmol/l)	coagulation time (h)	pH	First lower concentration below c_c (mmol/l)	PCCS ϕ_h (nm)
LiCl	5	120	6.7	4	554
NaCl	5	72	6.3	not measured	not measured
KCl	3	72	6.1	2	756
RbCl	3	120	6.5	2	582
CsCl	3	120	6.6	2	534

ϕ_h - mean hydrodynamic diameter

The C_C of univalent alkaline metal cations lies in range 2 to 5 mmol/l and their effect on coagulation is similar.

Issue: Colloid stability controlling processes - effect of anions

- Series of test-tube tests
  - The C_c of Na^+ and Mg^{2+} were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (only for 50 mg/l)
  - Different electrolytes (NaCl, $NaNO_3$, Na_2SO_4, Na_3PO_4 and $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$)

Salt	c_c (mmol/l)	$c_{c(cation)}$ (mekv/l)	pH	First lower concentration below c_c (mmol/l)	PCCS ϕ_h (nm)
NaCl	5	5	6.3	not measured	not measured
$NaNO_3$	6	6	6.0	5	870
Na_2SO_4	3	6	6.1	2	approx. 1000
Na_3PO_4	no coagulation at given phosphate concentrations				

Salt	c_c (mmol/l)	pH	First lower concentration below c_c (mmol/l)	PCCS ϕ_h (nm)
$MgCl_2$	0.5	6.7	0.1	790
$Mg(NO_3)_2$	0.5	6.4	0.1	500
$MgSO_4$	0.5	6.1	0.1	476

ϕ_h - mean hydrodynamic diameter

No significant effect of varying anions at given conditions was found.

Issue: Colloid stability controlling processes – complex system (groundwater)

- Comparison of the composition of SGW and the determined C_C values of selected ions

	Concentration in SGW		c_c of selected cation
	mg/l	**mmol/l**	**mmol/l**
Na	10.6	0.5	6
K	1.8	0.05	3
Ca	27	0.7	0.5
Mg	6.4	0.3	0.5

Synthetic granitic groundwater – composition based on groundwaters from granitic Bohemian Massif [1)]

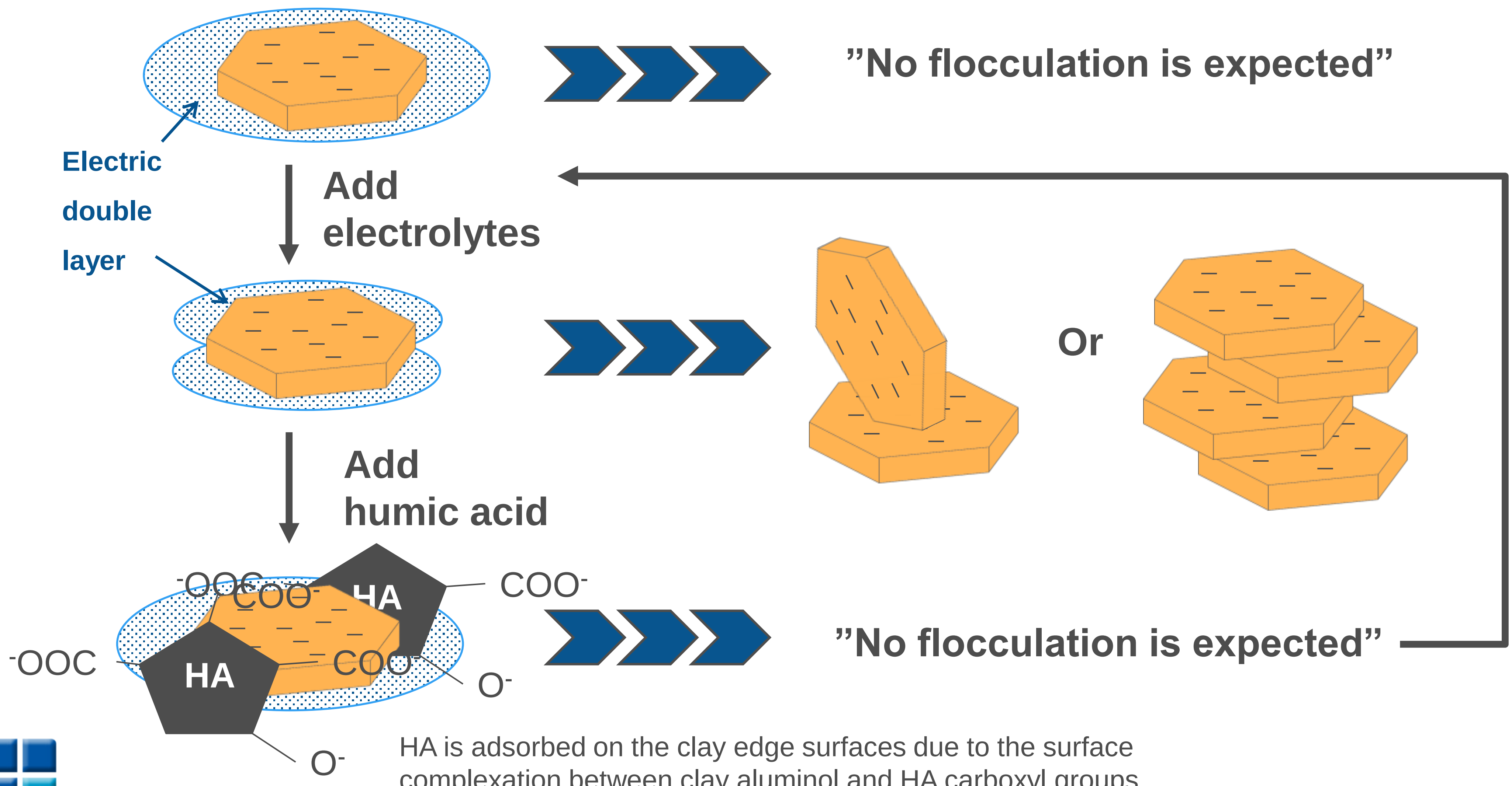
- Confirmation by coagulation experiments with suspension of purified bentonite B75 in Na^+ and raw bentonite BaM in SGW (three suspensions 500, 50 and 5 mg/l)

In complex system (e.g. groundwater), the coagulation effect of selected ions can be added up separately for the univalent ions, and divalent ions that are more effective coagulants. The coagulation tests in SGW for raw bentonite BaM and for B75 in Na^+ form demonstrated identical results. Colloid particles in these groundwater coagulate and settle.

1) Rukavičková et al., 2009. DZZ 3.3. Výzkum procesů pole vzdálených interakcí HÚ VJP a VAO. Czech report.

Issue: Influence of other factors to colloid stability - effect of humic acid

- Expectations:

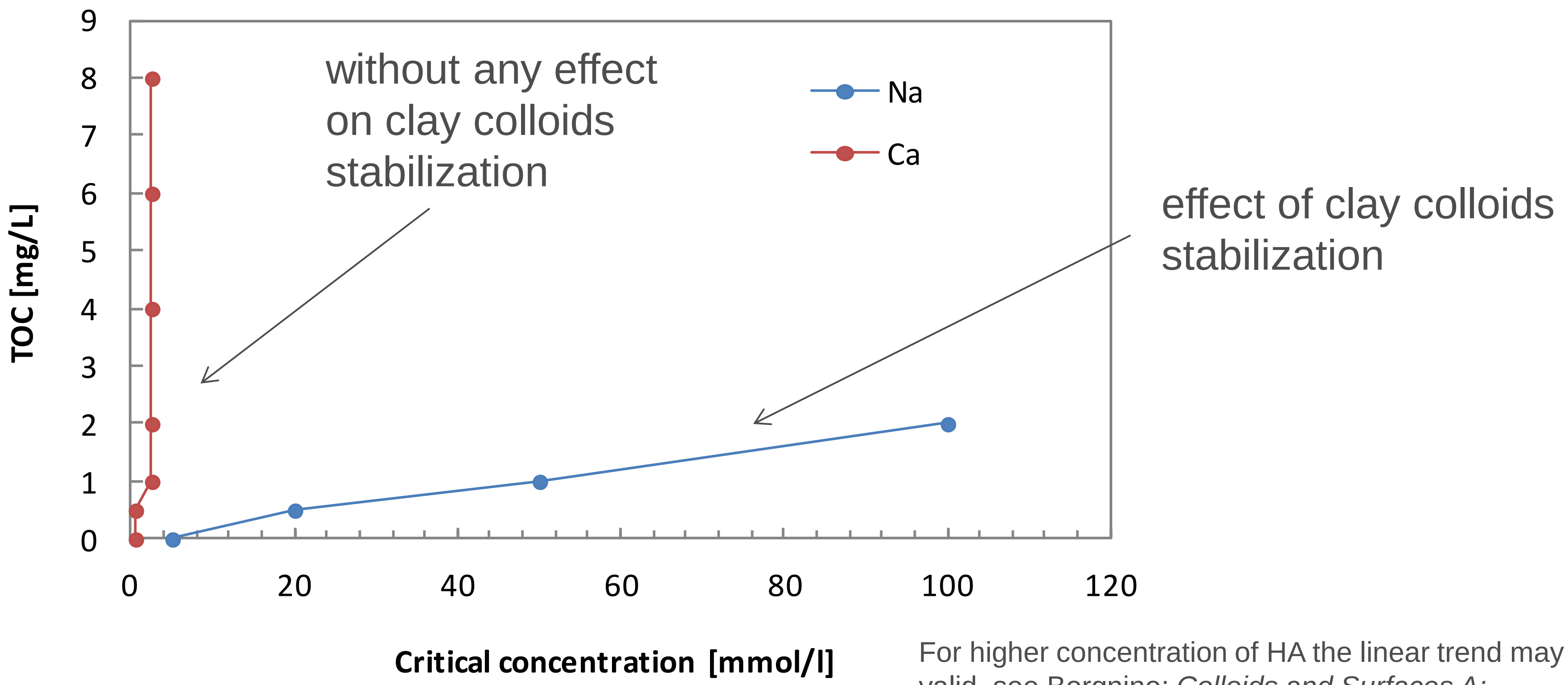


HA is adsorbed on the clay edge surfaces due to the surface complexation between clay aluminol and HA carboxyl groups.

Some pictures: Rasmus Eriksson, B+Tech Oy

Issue: Influence of other factors to colloid stability - effect of humic acid

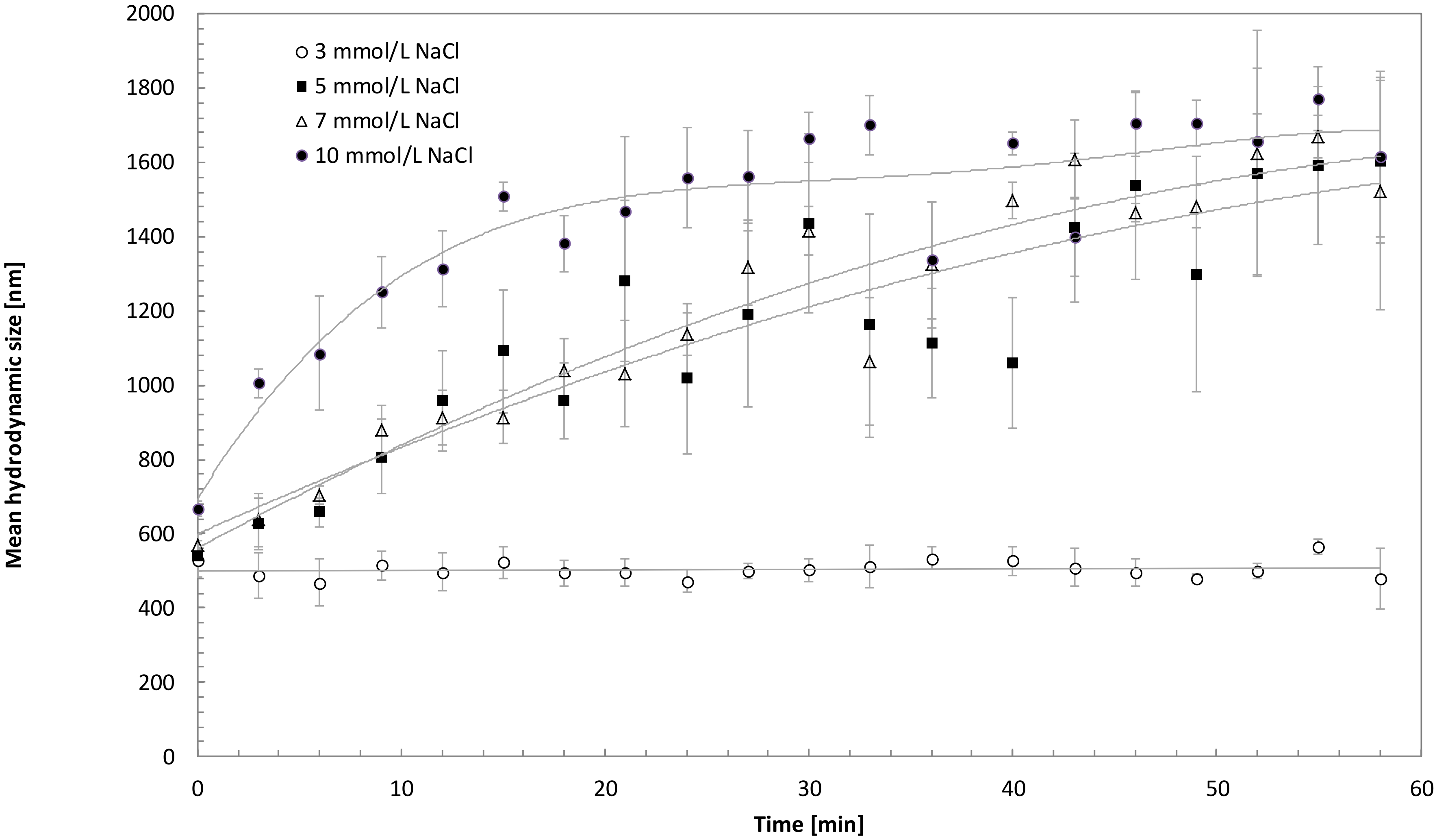
- Experimental results
  - The C_c of NaCl and $CaCl_2$ in presence of HA were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (only for 50 mg/l)
  - HA-12/3 concentrations expressed as mg/l of total organic carbon (TOC)



For higher concentration of HA the linear trend may not be valid, see Borgnino: *Colloids and Surfaces A: Physicochem. Eng. Aspects.* **2013**. 423, 178– 187.

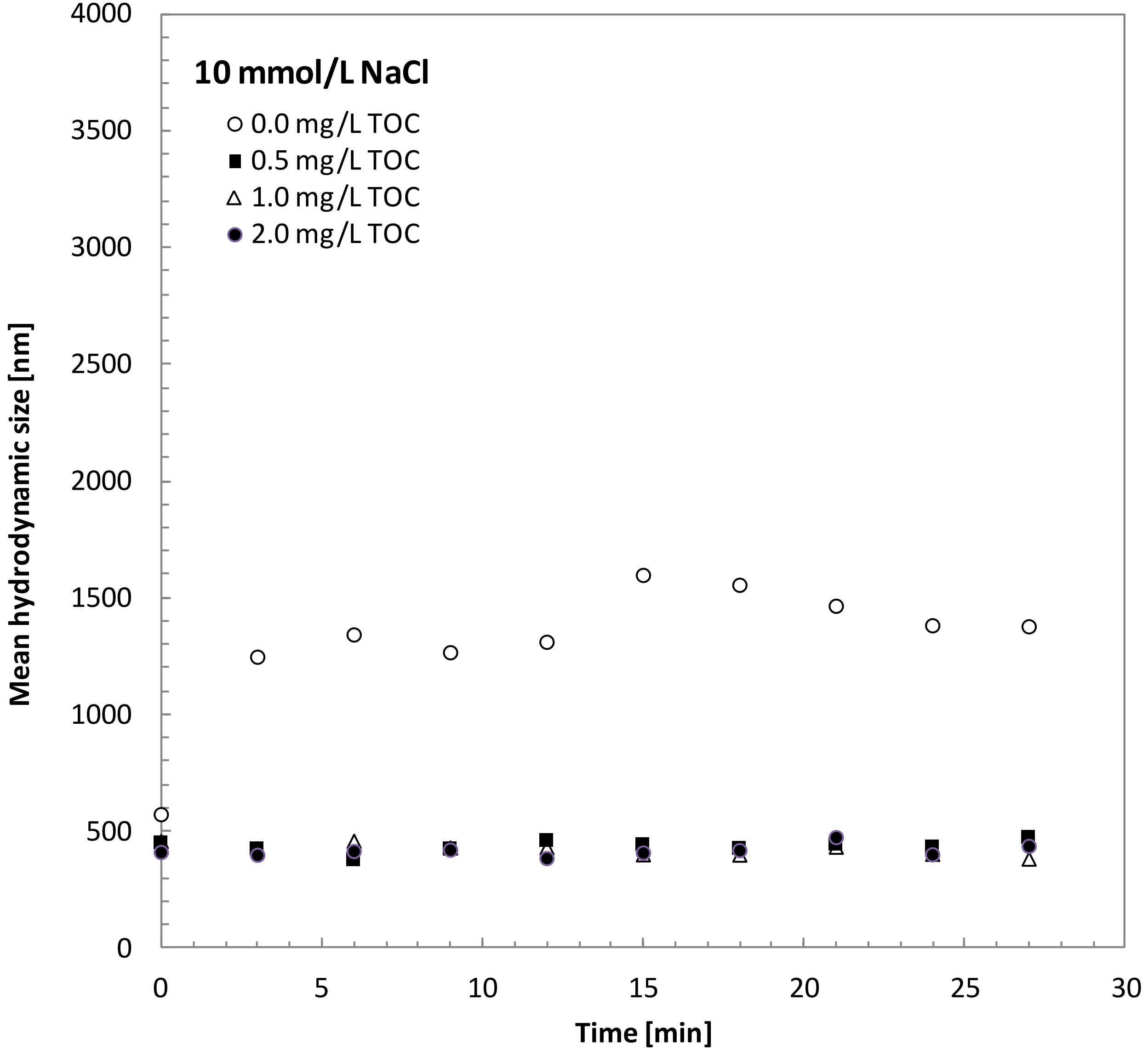
Issue: Colloid stability controlling processes – coagulation kinetics

Bentonite B75 in Na^+ as suspension in distilled water - 0.005 % w/w

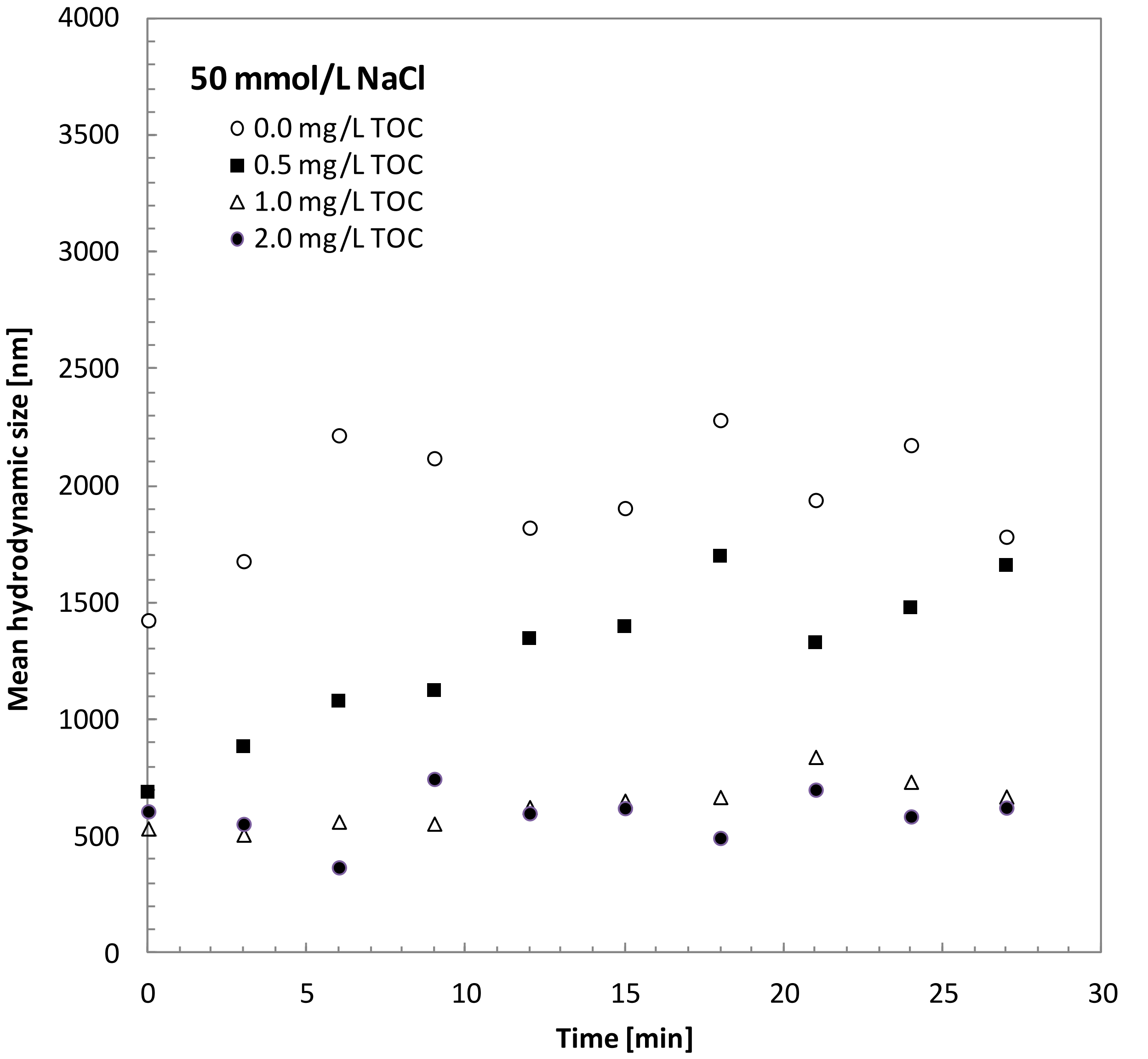


Below the CCC the mean hydrodynamic size does not change with time; above CCC the mean hydrodynamic size increases with time. The size change in a given time is dependent on electrolyte concentration. During the first 30 min. the size change is fast (fast coagulation) and decreases with time. After one hour the mean hydrodynamic size is quite similar for all electrolyte concentrations and particles aggregation is slow.

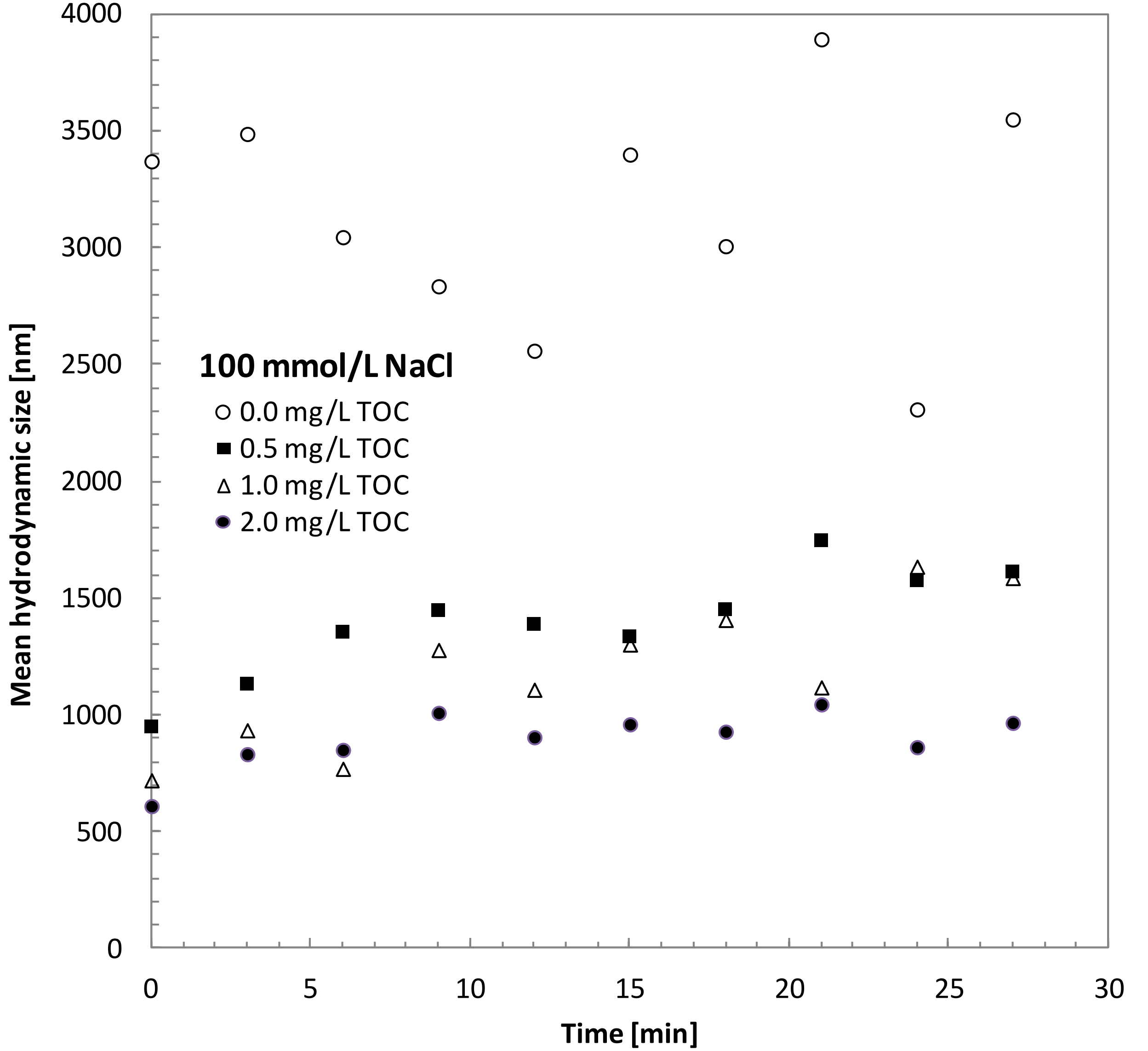
Issue: Colloid stability controlling processes – coagulation kinetics + humic acid



Issue: Colloid stability controlling processes – coagulation kinetics + humic acid



Issue: Colloid stability controlling processes – coagulation kinetics + humic acid



Acknowledgement

- The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.