BELBaR Project

Coagulation behaviour of clay dispersions in simple electrolytes – consequences for the possible real groundwater

WP4

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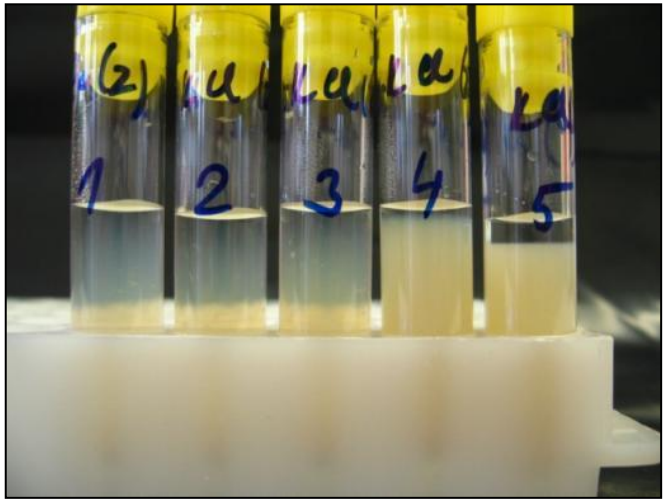
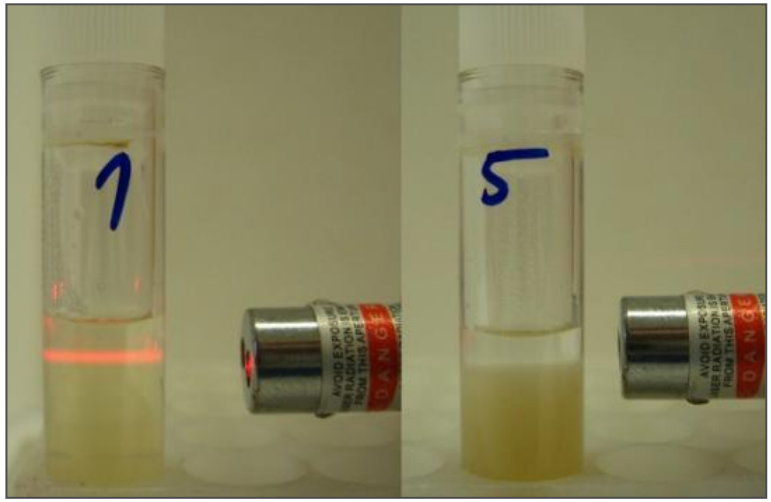
Objectives of coagulation studies

- The coagulation experiments with dilute clay suspensions are performed mainly for prediction of colloids stability during the transport in the far field
  - The chemistry of groundwater has dominant impact on clay colloids stability and therefore the potential influence of relevant Czech granititc groundwaters from Bohemian Massif was studied

Coagulation of clay dispersions by inorganic cations – previous results

- 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)





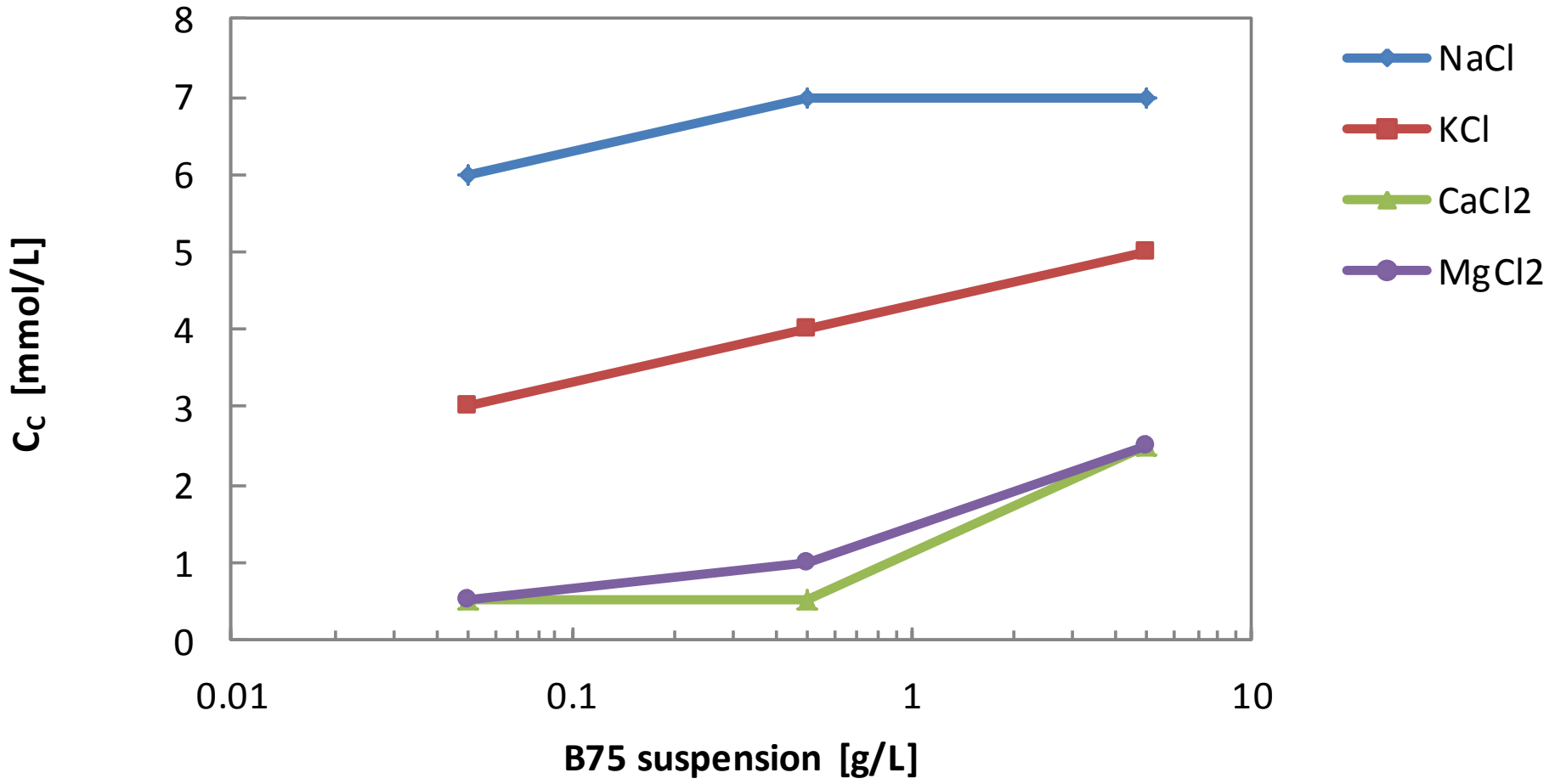
1} Berg J. C. (2010). An Introduction to Interfaces and Colloids: The Bridge to Nanoscience. World Scientific Publishing Co. Pte. Ltd., Singapore, 785 pp.

Coagulation of clay dispersions by inorganic cations – previous results

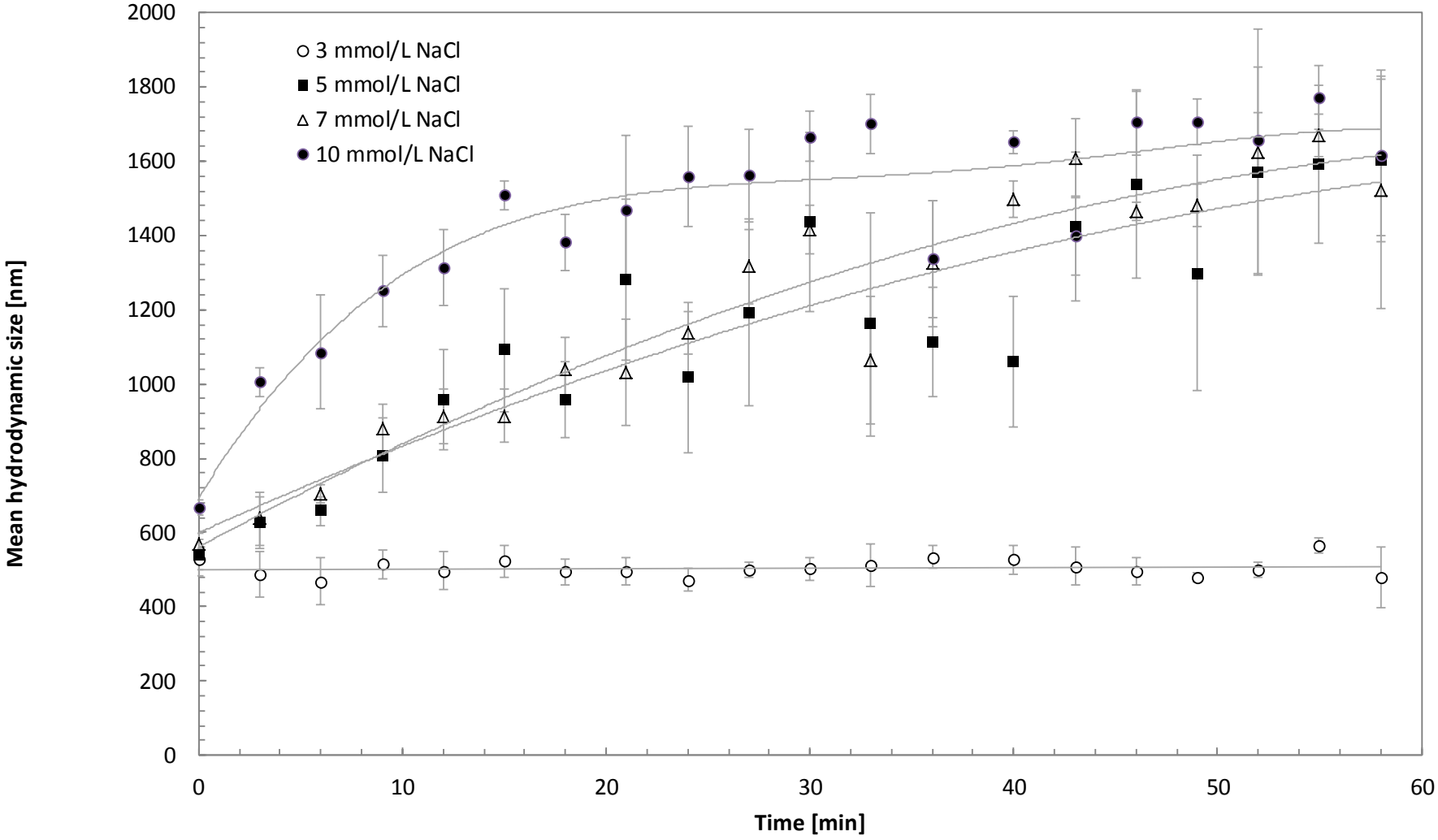
- Does the cation exchange influence the C_C?
  - For dilute clay suspensions (up to 5g/l), the effect of cation exchange on C_C was not observed

	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

Coagulation of clay dispersions by inorganic cations – previous results



Coagulation kinetics of clay dispersions by inorganic cations – previous results



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

Coagulation of clay dispersions by inorganic cations (Na^+, K^+, Li^+, Cs^+, Rb^+ and Ca^{2+}, Mg^{2+})

- 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

Coagulation of clay dispersion by inorganic cations (Na^+ and Mg^{2+}) - 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

Coagulation of clay dispersion by inorganic cations (Na^+, Ca^{2+}) - effect of humic acid

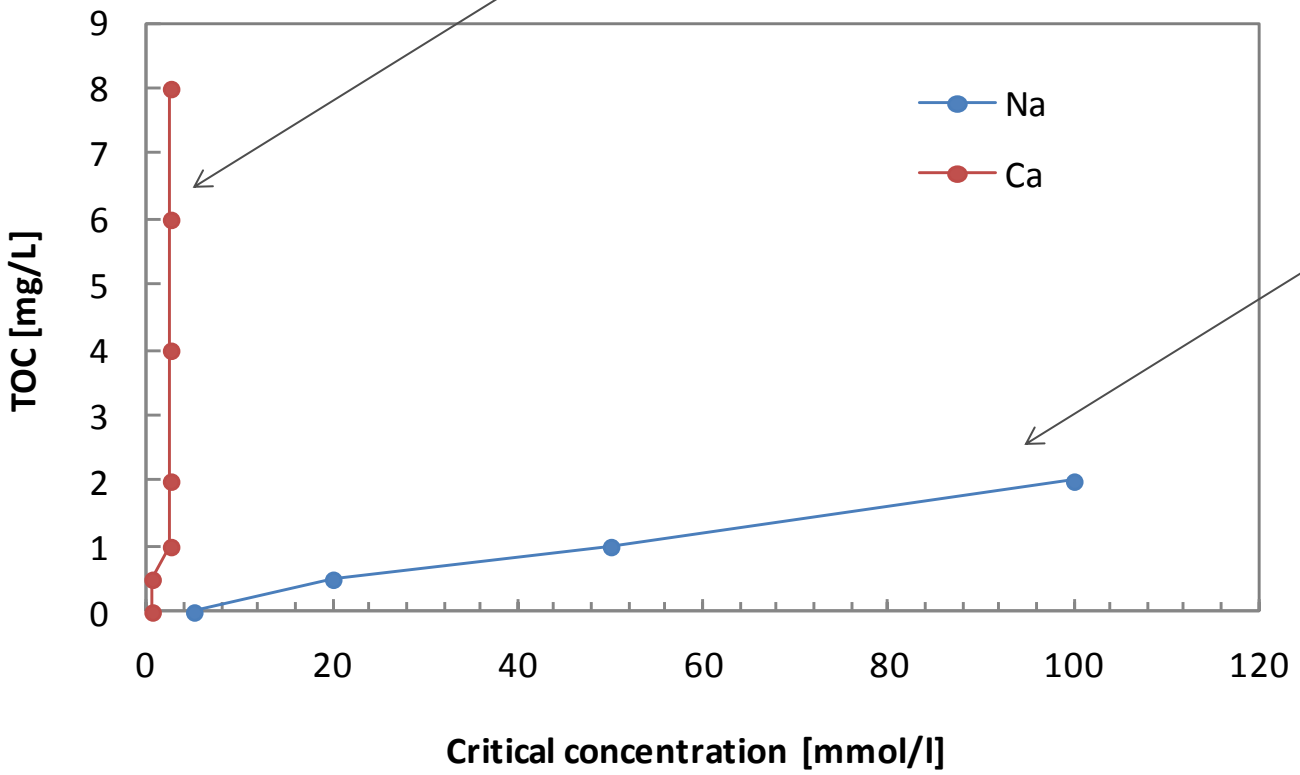
- Series of test-tube tests
  - The C_c of NaCl and $CaCl_2$ in presence of HA were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (only for 50 mg/l)
  - HA-12/3 concentrations expressed as mg/l of total organic carbon (TOC)

Salt	c_c (mmol/l)	Humic acid (mg/l)	pH	First lower concentration below c_c (mmol/l)	PCCS ϕ_h (nm)
NaCl	20	0.5	6.5	10	not measured
NaCl	50	1	6.3	20	not measured
NaCl	100	2	6.4	50	not measured
$CaCl_2$	0.5	0.5	6.6	not measured	not measured
$CaCl_2$	2.5	1	6.2	0.5	722
$CaCl_2$	2.5	2	6.8	0.5	530
$CaCl_2$	2.5	4	6.8	0.5	496
$CaCl_2$	2.5	6	7.1	0.5	482
$CaCl_2$	2.5	8	7.4	0.5	427

ϕ_h - mean hydrodynamic diameter

Coagulation of clay dispersion by inorganic cations (Na^+, Ca^{2+}) - effect of humic acid

without any effect on clay colloids stabilization



effect of clay colloids stabilization

Coagulation behaviour of clay dispersions in synthetic granitic groundwater (SGW)

- 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)

- The bentonite colloids are not stable in the potential groundwater

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

Summary and conclusions

- The C_C of univalent alkaline metal cations lies in range 2 to 5 mmol/l and their effect on coagulation is similar.
- No significant effect of varying anions at given conditions was found.
- The presence of HA significantly increases the colloidal stability of bentonite particles in case of NaCl electrolyte. In case of $CaCl_2$ electrolyte only minor effect occurred. It seems that the stabilizing effect of humic acid is different for univalent and divalent cations.
- 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.

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