BELBaR Project

COAGULATION BEHAVIOUR OF CLAY DISPERSIONS IN PRESENCE OF VARIOUS CATIONS, ANIONS AND ORGANIC MATTER

WP4

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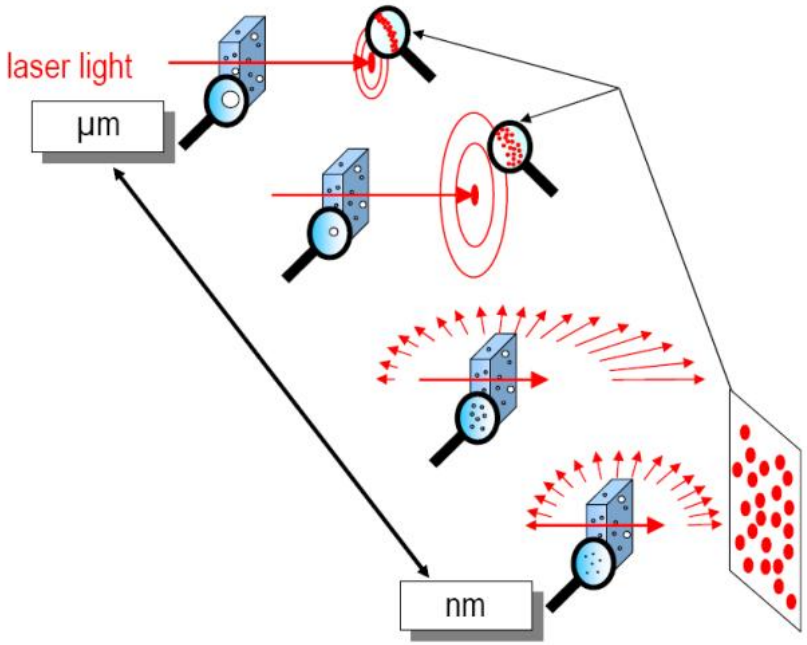
Objectives of coagulation studies

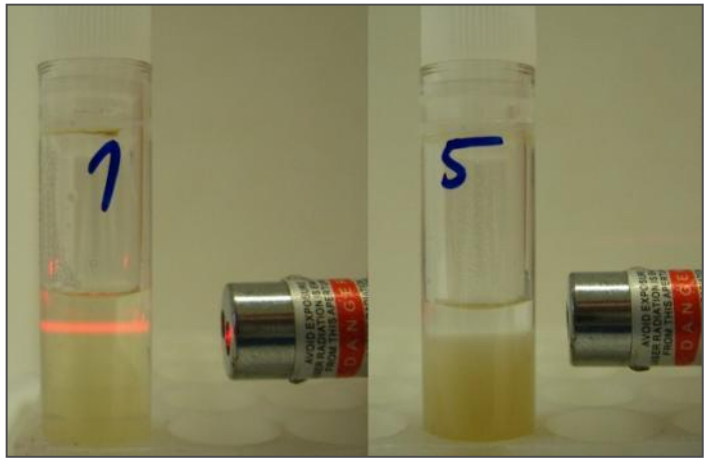
- The coagulation experiments with dilute clay suspensions are performed mainly for prediction of colloids stability during the transport in the far field.
  - The chemistry of groundwater has dominant impact on clay colloids stability and therefore the potential influence of relevant Czech granititc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

- The obtained critical coagulation concentrations (CCC) for coagulants in dilute systems can be transferred to much more dense systems (erosion task), but with some limitations (e.g. effect of cation exchange, clay origin and structure, hysteresis).

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

- Series of test-tube tests
  - The CCC 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.

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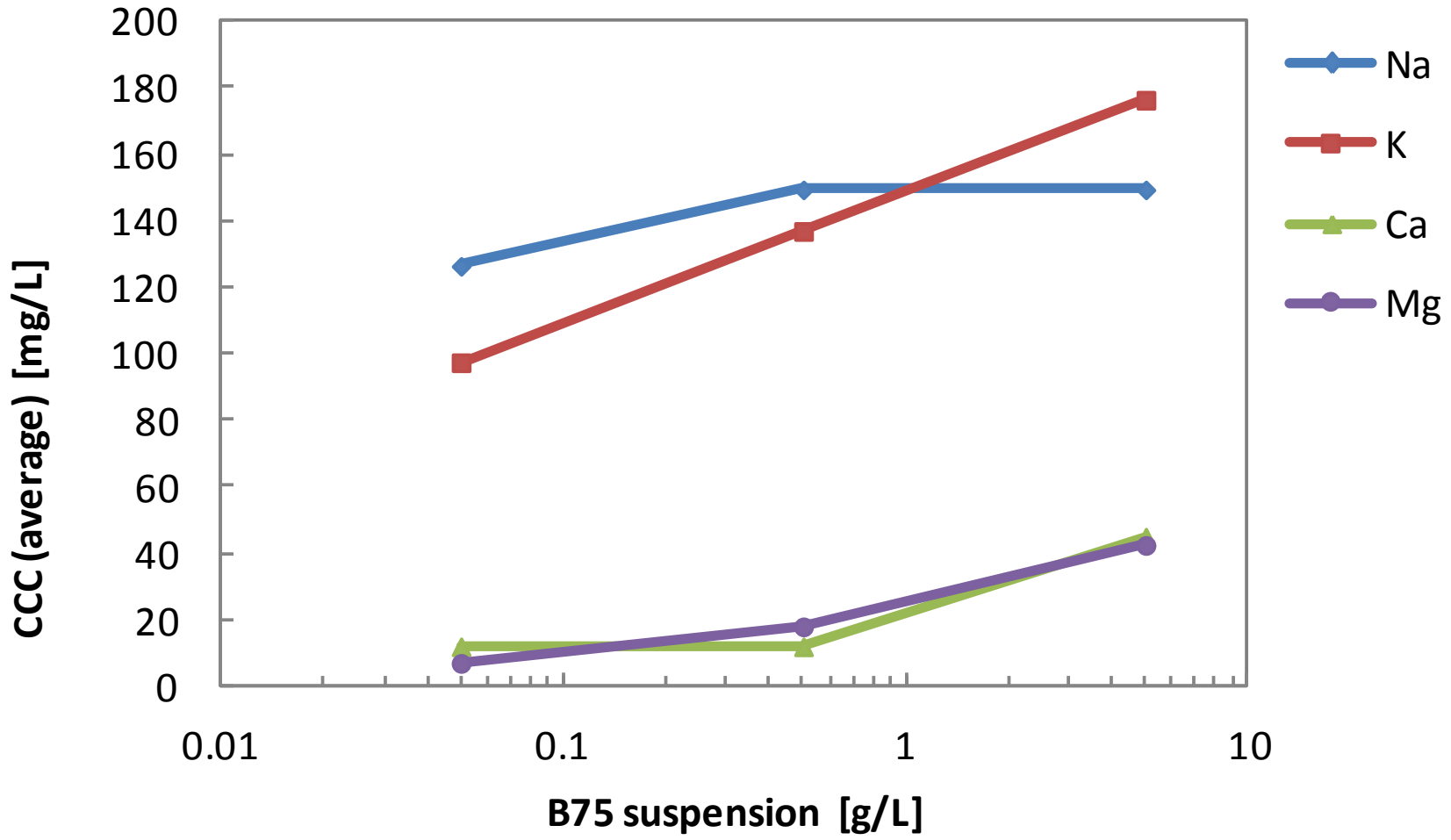


Coagulation of clay dispersions by inorganic cations (Na^+, K^+, Ca^{2+}, Mg^{2+})

- How the cation exchange influences the CCC?
  - For dilute clay suspensions (up to 5g/l), the effect of cation exchange on CCC 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 (Na^+, K^+, Ca^{2+}, Mg^{2+})

Groundwaters from granitic Bohemian Massif [1)]

Component		Na	K	Ca	Mg	F	Cl	SO_4	HCO_3	NO_3
SGW	**mg/l**	10.6	1.8	27.0	6.4	0.2	42.4	27.7	30.4	6.3
	mmol/l	0.5	0.0	0.7	0.3	0.0	1.2	0.3	0.5	0.1
Groundwater	**mg/l**	11.4	2.3	30.1	8.0	-	11.7	34.1	85.4	-
(median, n > 351)	**mmol/l**	0.5	0.1	0.8	0.3	-	0.3	0.4	1.4	-
Mineral groundwater	**mg/l**	501.5	25.5	60.9	28.7	-	92.6	162.5	1220.5	-
(median, n = 16)	**mmol/l**	21.8	0.7	1.5	1.2	-	2.6	1.7	20.0	-
Fossil groundwater	**mg/l**	1050.0	52.5	55.9	22.0	-	644.0	26.3	863.0	-
(median, n = 15)	**mmol/l**	45.7	1.3	1.4	0.9	-	18.2	0.3	14.1	-
CCC for selected cations		**Na**	**K**	**Ca**	**Mg**					
0.5 % w/w	**mg/l**	138-161	157-196	40-100	24-61	-	-	-	-	-
	mmol/l	6-7	4-5	1-2.5	1-2.5	-	-	-	-	-
0.05 % w/w	**mg/l**	138-161	117-157	4-20	12-24	-	-	-	-	-
	mmol/l	6-7	3-4	0.1-0.5	0.5-1	-	-	-	-	-
0.005 % w/w	**mg/l**	115-138	78-117	4-20	2-12	-	-	-	-	-
	mmol/l	5-6	2-3	0.1-0.5	0.1-0.5	-	-	-	-	-

- The bentonite colloids are not stable in the potential groundwaters.

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

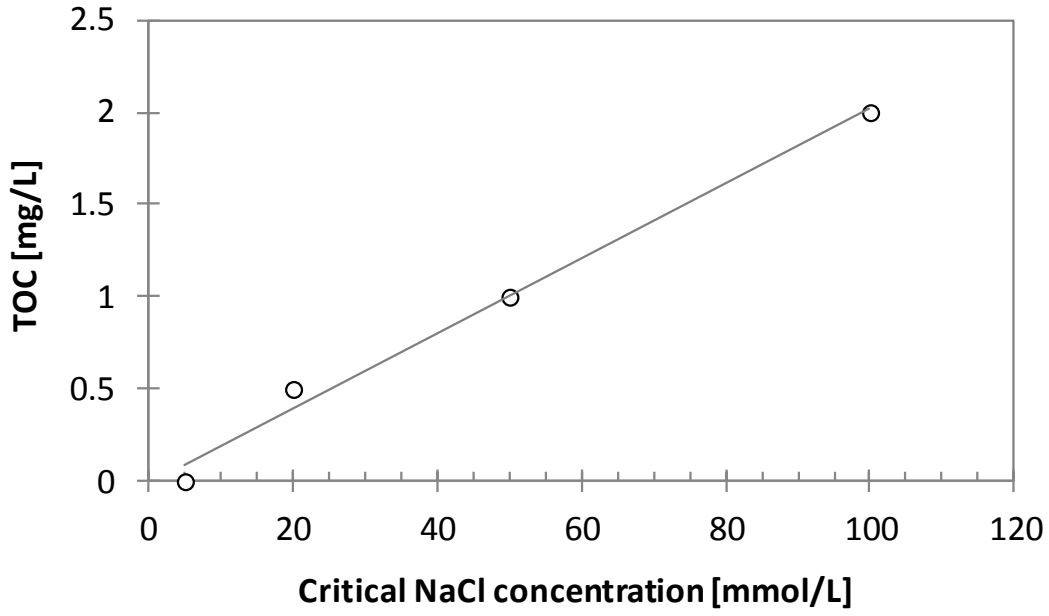
Coagulation of clay dispersion by inorganic cations (Na^+ and Mg^{2+}) - effect of anions

- Series of test-tube tests
  - The CCC 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 0.005 % w/w)
  - Different electrolytes (NaCl, $NaNO_3$ and Na_2SO_4 and $MgCl_2$, $Mg(NO_3)_2$ and $MgSO_4$)

- Results
  - For electrolytes NaCl, $NaNO_3$ and Na_2SO_4 the appropriate CCC were 5, 6 and 3 mmol/l with corresponding ionic strength 5, 6 and 9 mmol/l.
  - For $MgCl_2$, $Mg(NO_3)_2$ and $MgSO_4$ the CCC were exactly the same 0.5 mmol/l with corresponding ionic strength 1.5, 1.5 and 2 mmol/l.

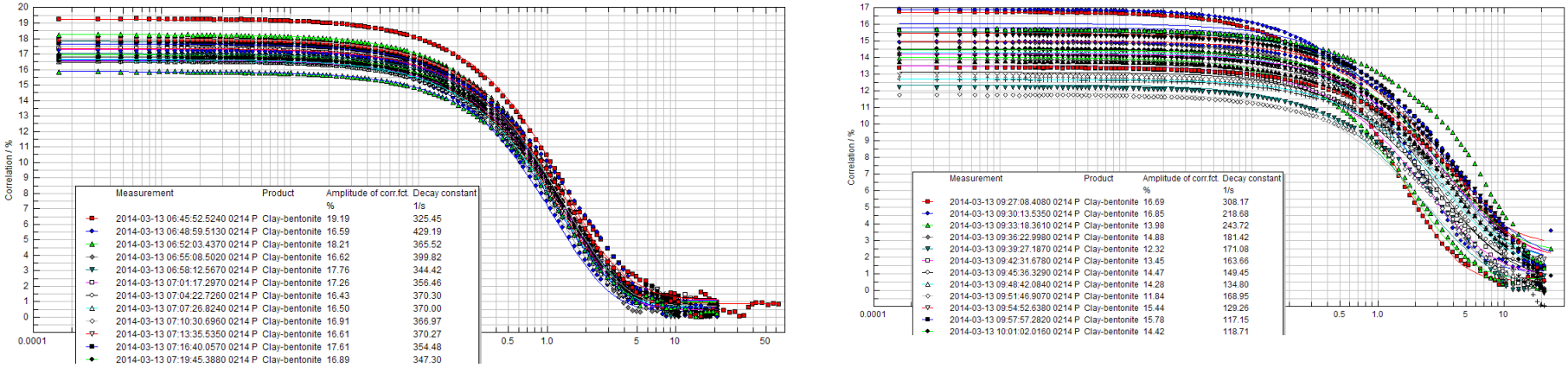
Coagulation of clay dispersion by inorganic cations (Na^+) - effect of humic acid

- Series of test-tube tests
  - The CCC of Na+ in presence of HA were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (only 0.005 % w/w)
  - NaCl electrolyte concentrations 10 to 500 mmol/l
  - HA concentrations 0 to 2 mg/l of total organic carbon (TOC)
  - The final solutions pH varied from 5.9 to 6.7



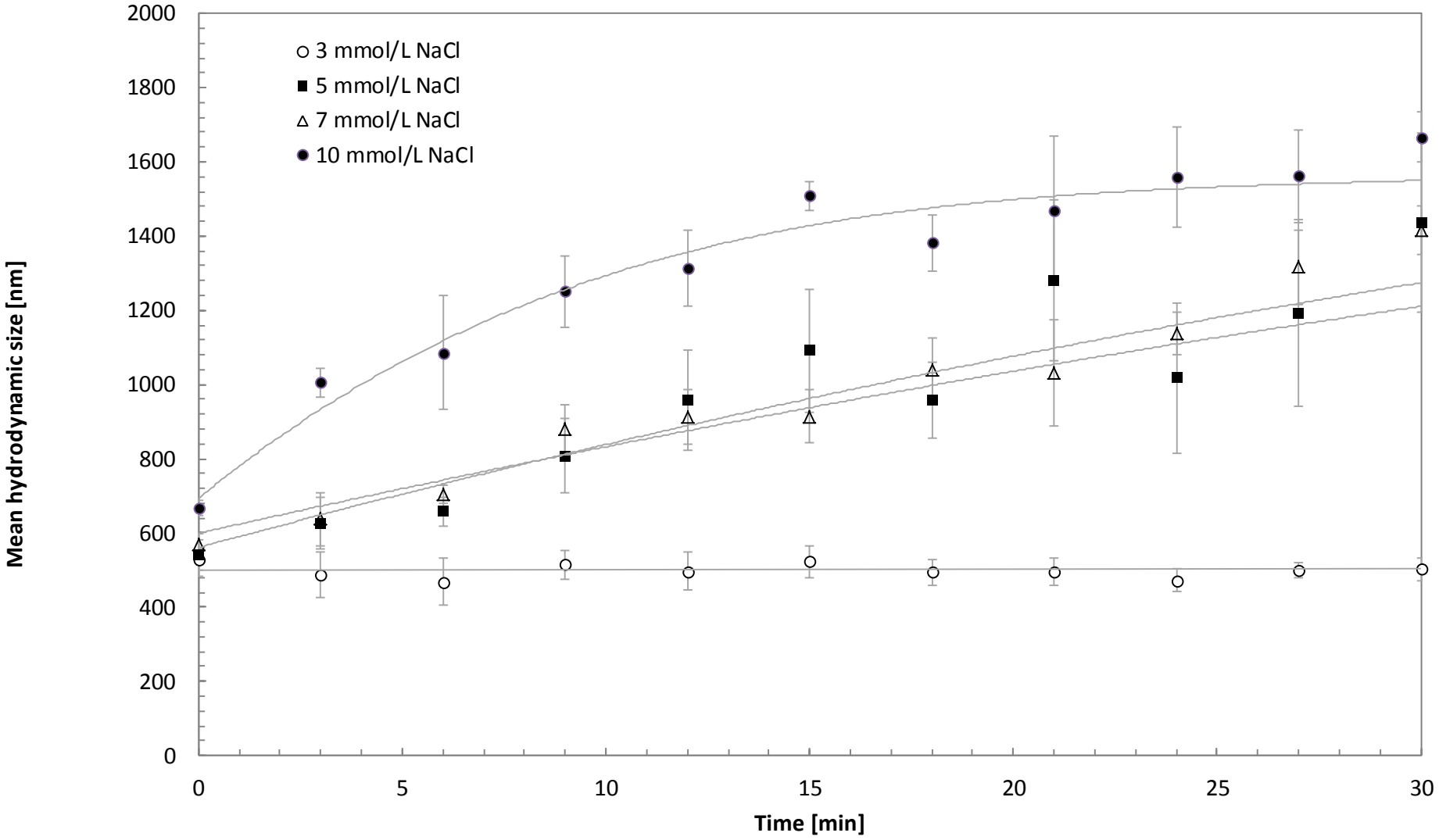
Coagulation kinetics of clay dispersion in presence of NaCl electrolyte

- Coagulation kinetics - follow the increase in average hydrodynamic radius with time as the particles undergo coagulation
  - Bentonite B75 in Na^+ as suspension in distilled water (only 0.005 % w/w)
  - NaCl electrolyte concentrations 3, 5, 7 and 10 mmol/l
  - The hydrodynamic particle radius was monitored over time period of 1 hour recording the cross-correlation function every 3 minutes (1 minute of measuring and 2 minutes of pause)
  - Measured by PCCS, data evaluation with method of 2nd cumulant



Correlation function for bentonite suspension (0.005 % w/w) and 3 mmol/l (left) and 7 mmol/l (right) NaCl electrolyte.

Coagulation kinetics of clay dispersion in presence of NaCl electrolyte



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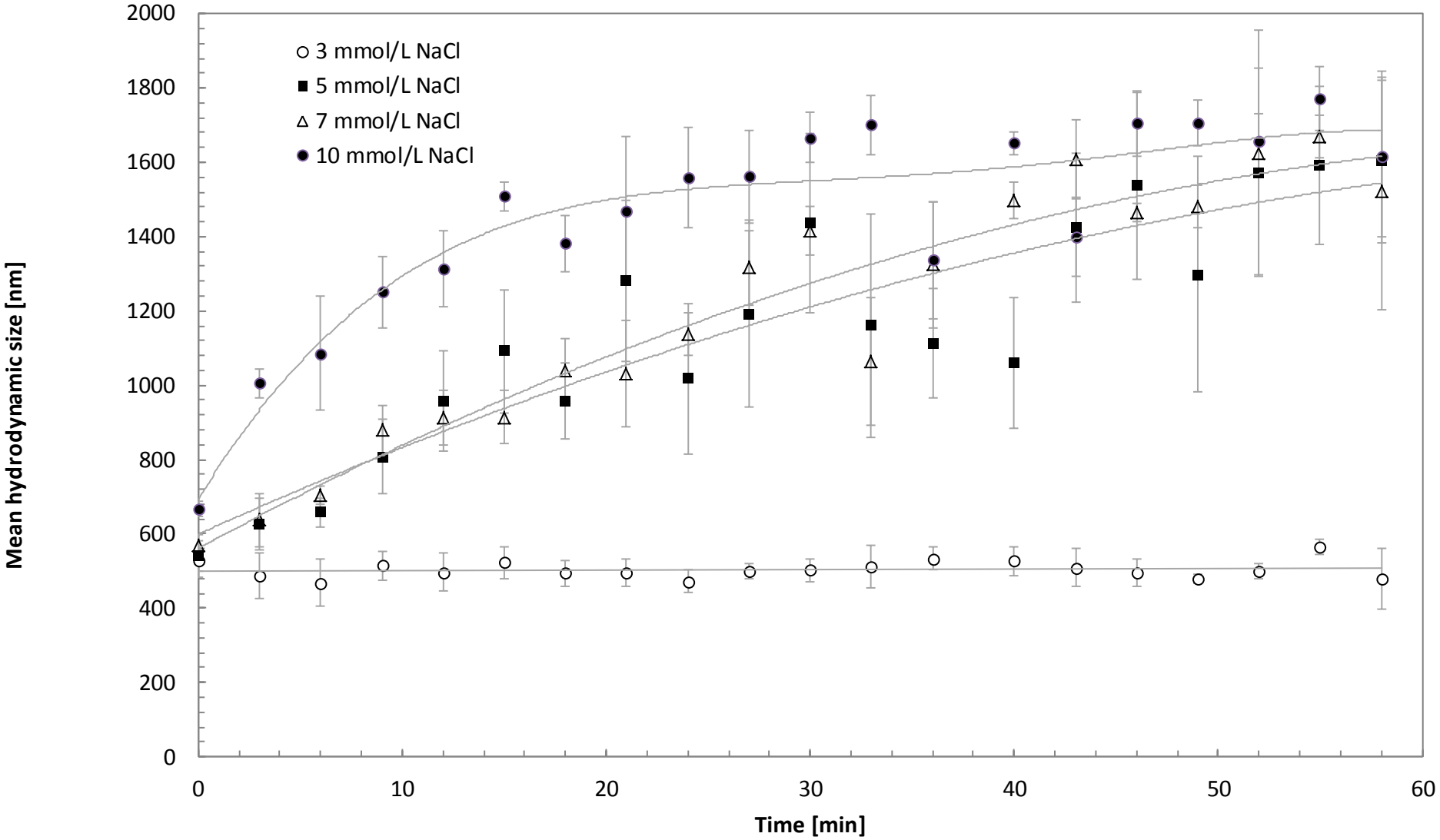
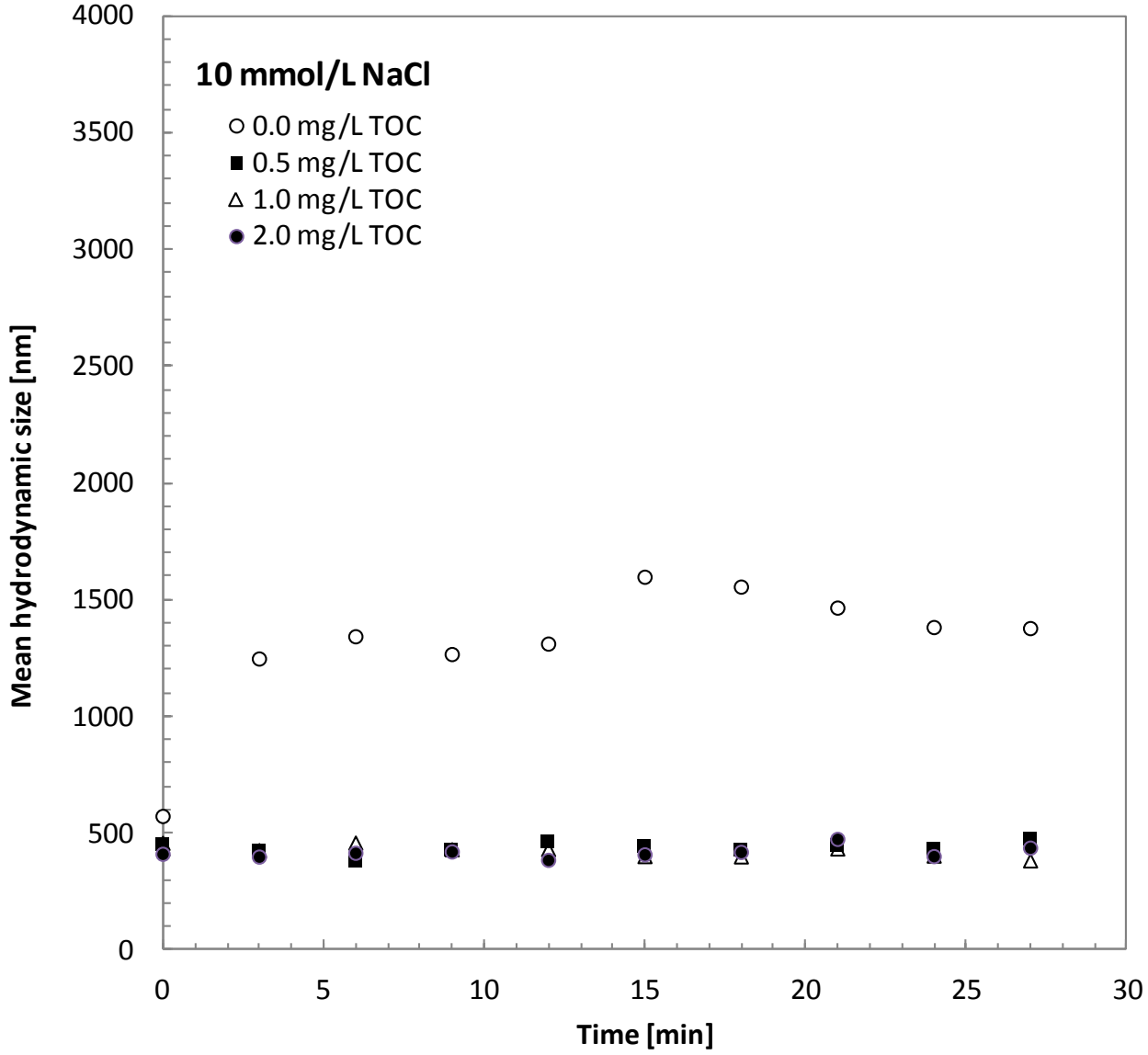


Coagulation kinetics of clay dispersion in presence of NaCl electrolyte and humic acid



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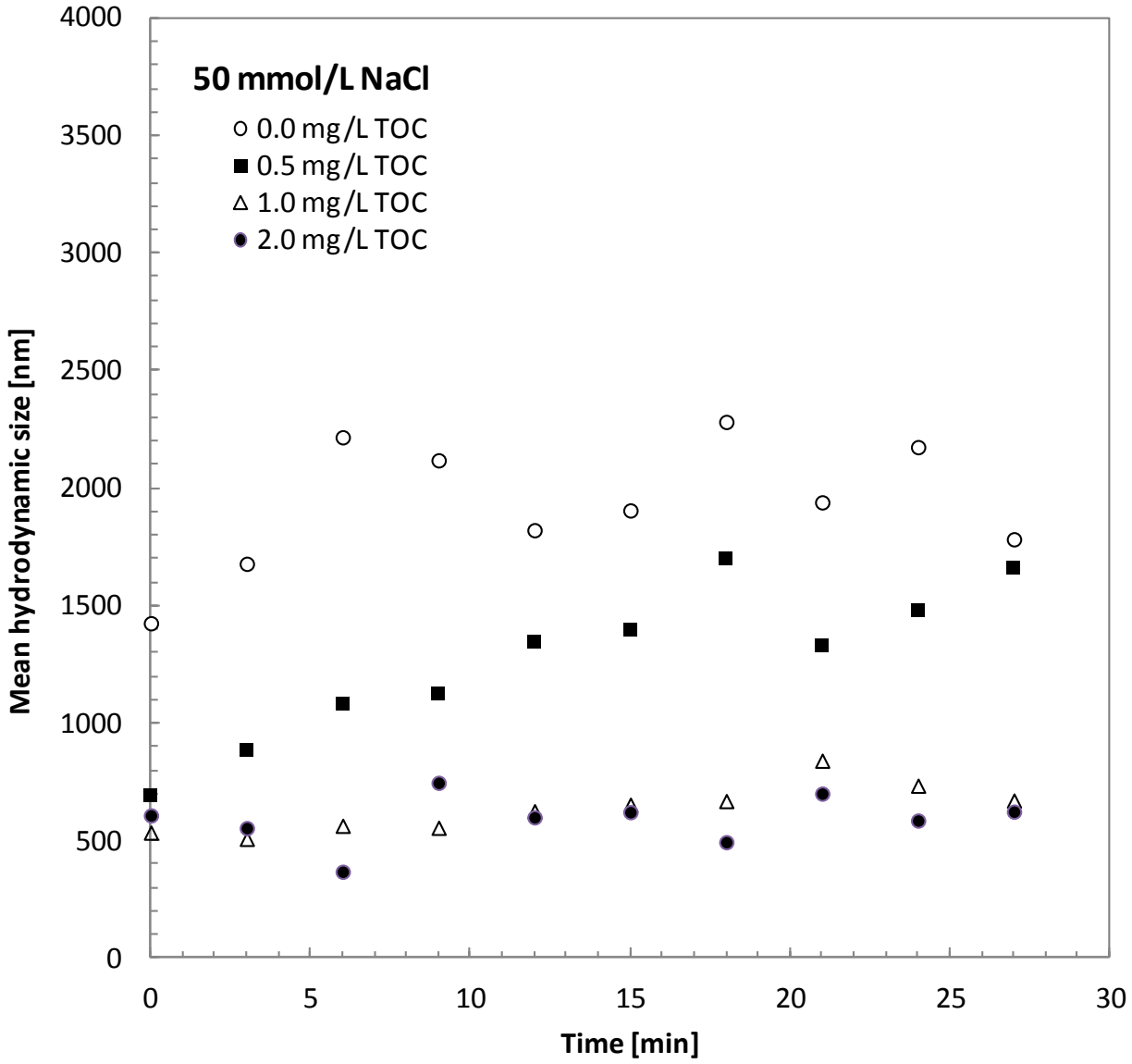

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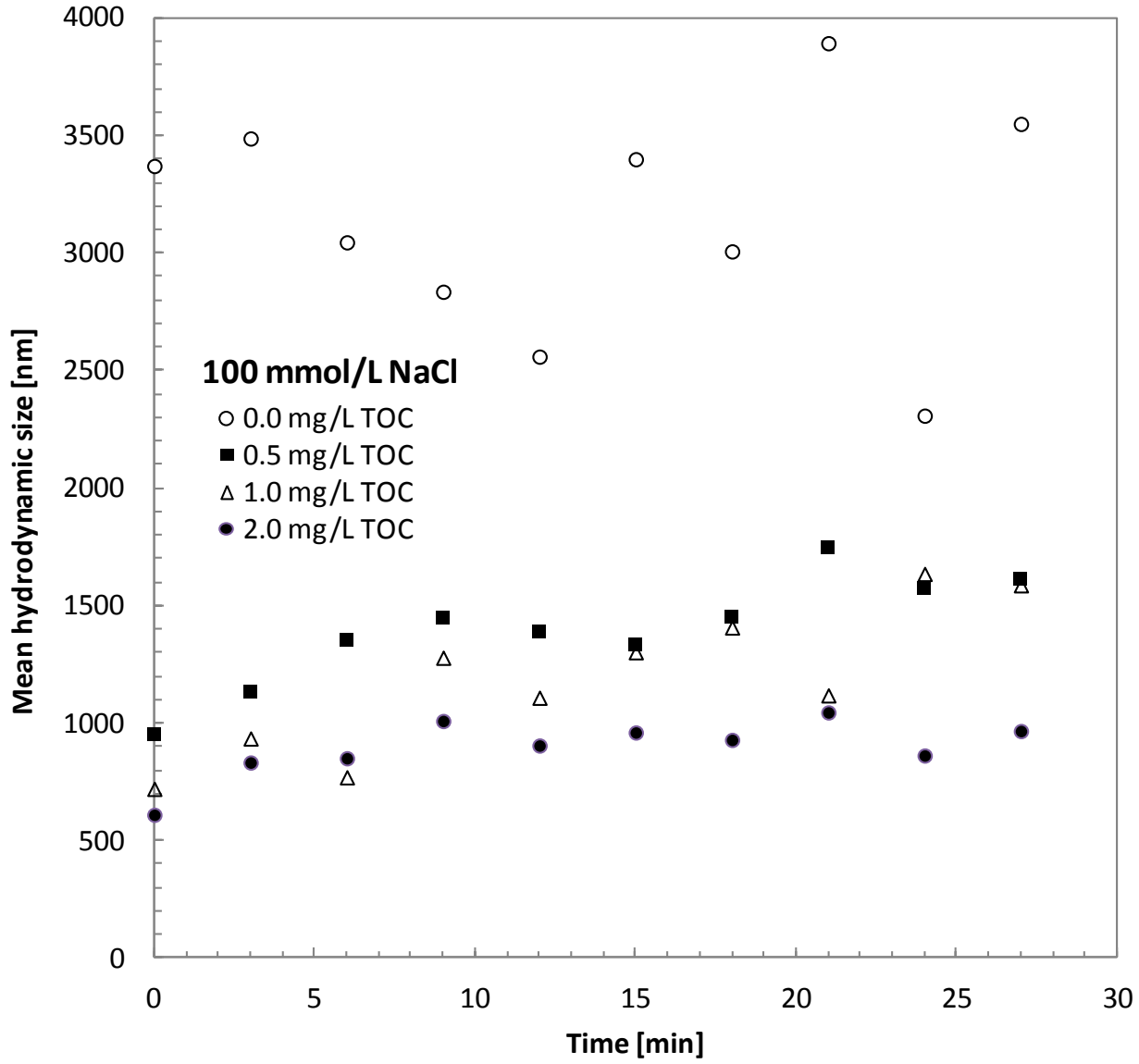

Summary and conclusions

- Comparison of obtained CCC values for cations with concentrations of these cations in different types of granitic groundwaters lead to the conclusion, that these groundwaters are not suitable for stability of clay colloids even for dense bentonite suspensions. This was confirmed by test of clay colloids stability in SGW. Also the same coagulation tests in SGW for raw bentonite BaM demonstrated almost identical results as for B75 in Na^+ form. Colloid particles in these groundwaters coagulate and settle.

- The presence of HA significantly increases the colloidal stability of bentonite particles, which also means, that in presence of HA the more concentrated NaCl electrolyte is needed for coagulation of clay dispersion (the CCC is higher).

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