BELBaR Project

Basic properties and coagulation of clay dispersions by inorganic cations: Czech Rokle Bentonite

WP4

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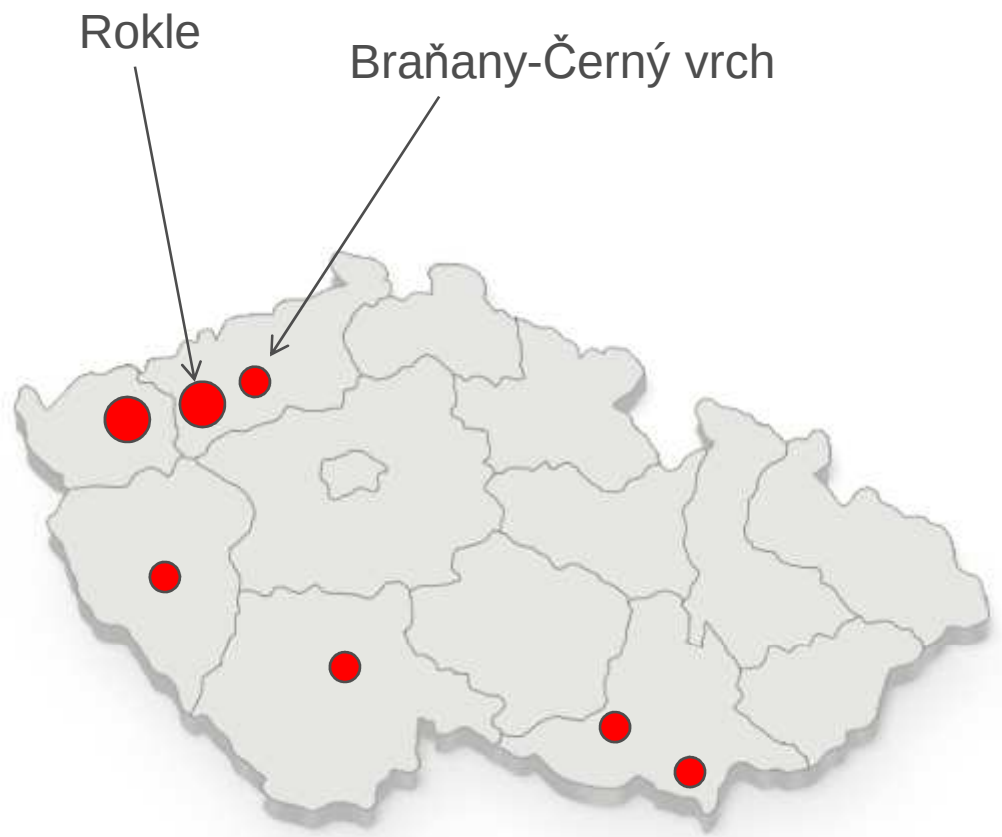
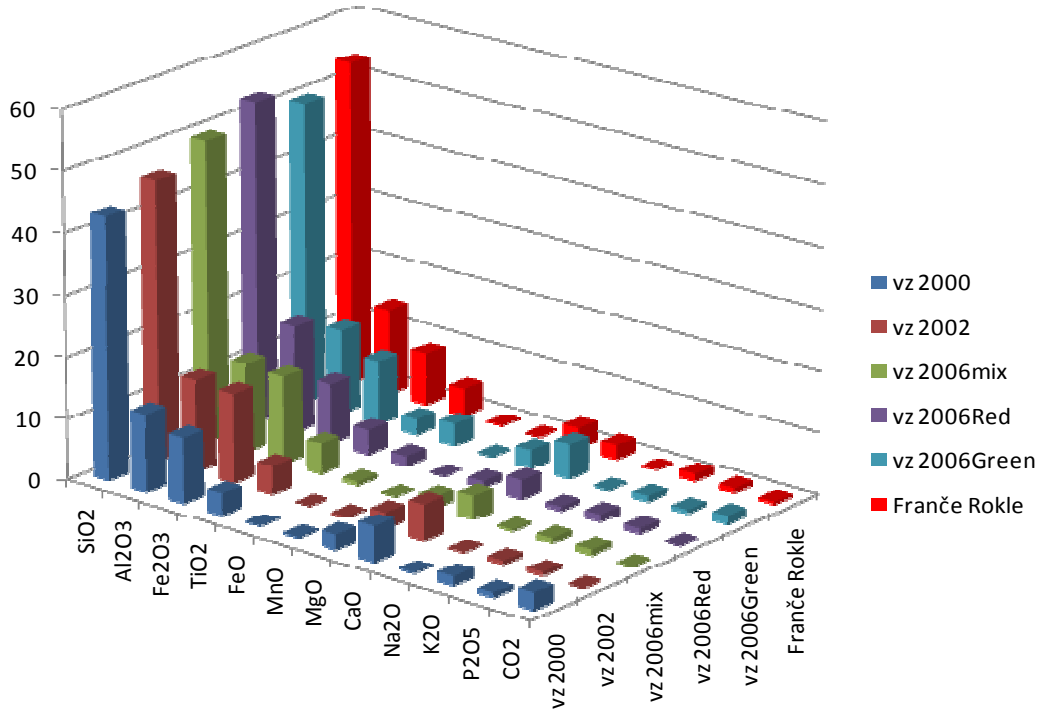
Czech bentonite deposits



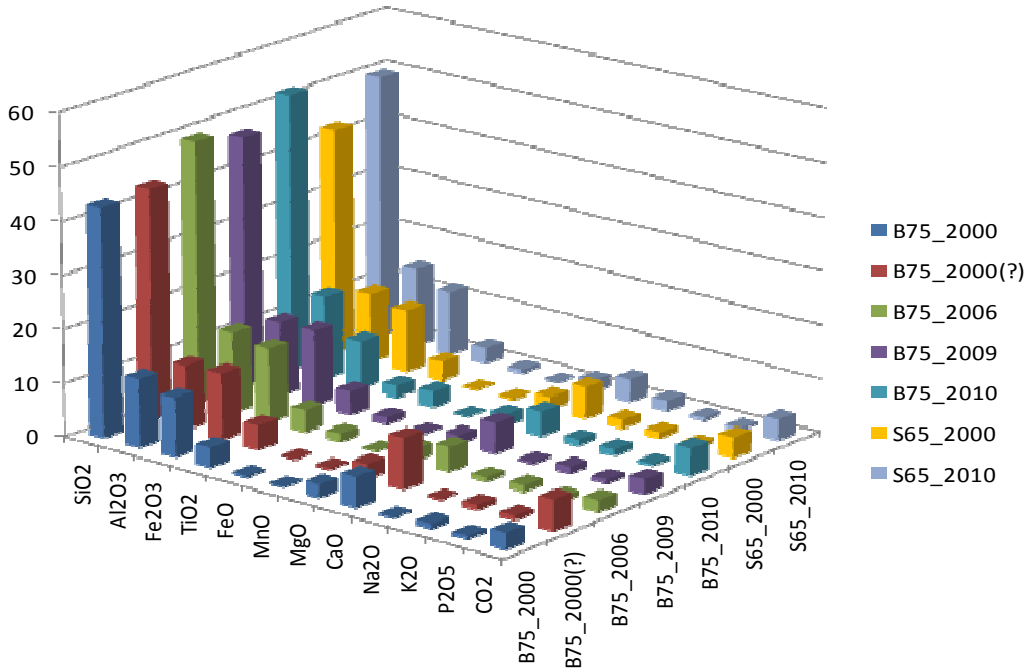
- Operating bentonite deposits (4/31)
  - Božíčany-Osmosa-jih
  - Braňany-Černý vrch
  - Maršov u Tábora
  - Rokle (44 mil. t.)
    - Stock in total 304 mil. t. (y 2010)
- Rokle
  - Rokle bentonite (Tertiary neovolcanic area, NW Bohemia) is Ca-Mg bentonite representing by a complex mixture of (Ca,Mg)-Fe-rich montmorillonite, micas, kaolinite and other mineral admixtures (mainly Ca, Mg, Fe carbonates, feldspars and iron oxides).
  - Commercial product (partly Na-activated) denoted as Bentonite 75 (B75).

Czech bentonite deposits (Rokle)

- In the last decade, the chemical variability of natural and commercial Rokle bentonites is quite stable, major differences are in the mineralogical composition and swelling minerals content.



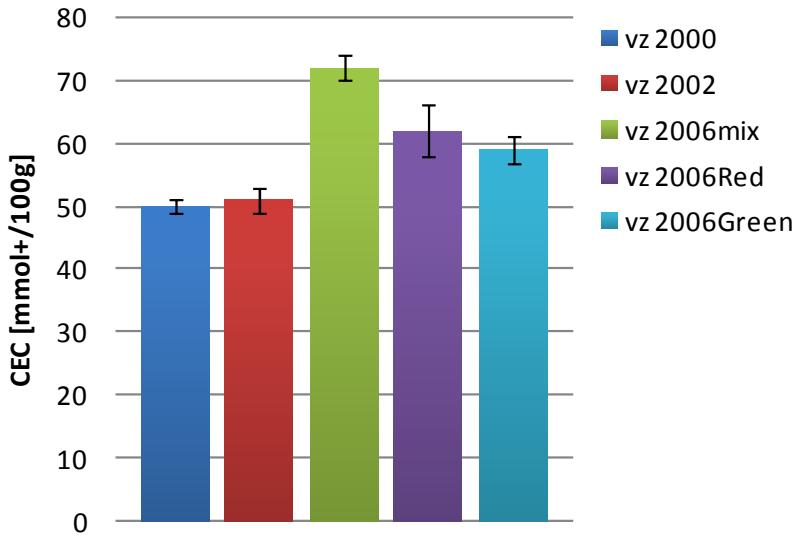
Natural Rokle bentonites



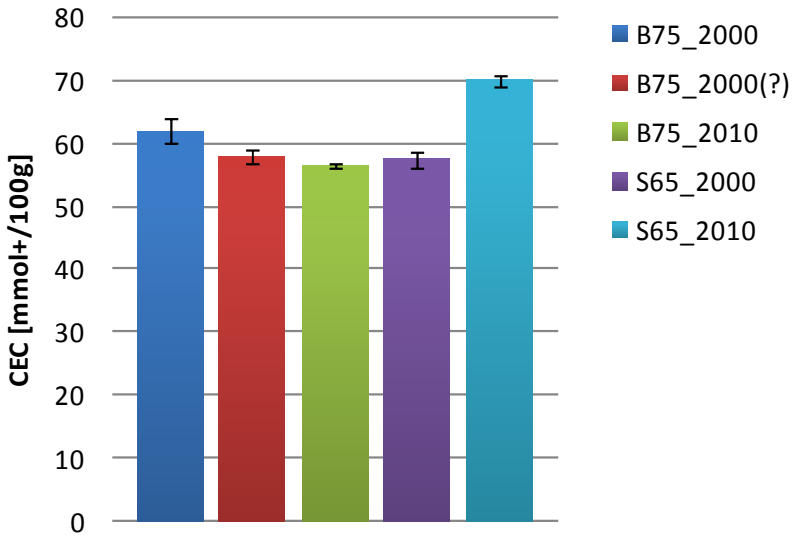
Commercial Rokle bentonite products

Czech bentonite deposits (Rokle)

- The amount of swelling minerals (mainly montmorillonite) varies from ~ 50 to ~ 75 wt. %, similarly as a cation exchange capacity (CEC) ~ 50 to ~ 75 meq/100g for both natural and commercial bentonites.



Natural Rokle bentonites



Commercial Rokle bentonite products

Purification of bentonite

- Purification of bentonite B75

Carbonates removal	sodium acetate-acetic acid buffer
Iron removal	sodium dithionite in acetic acid buffer / washed by NaCl
Fractionation by sedimentation	washed by pure water, fract. < 2 μm-fraction
Transfer to homoionic form - Ca/Na	NaCl/$CaCl_2$ washed by pure water
Dialysis	conductivity < 10μS/cm
Drying / lyofilization	final product bentonite in Na^+ or Ca^{2+} form

Purification of bentonite

Bentonite after lyofilization – stereomicroscope pictures

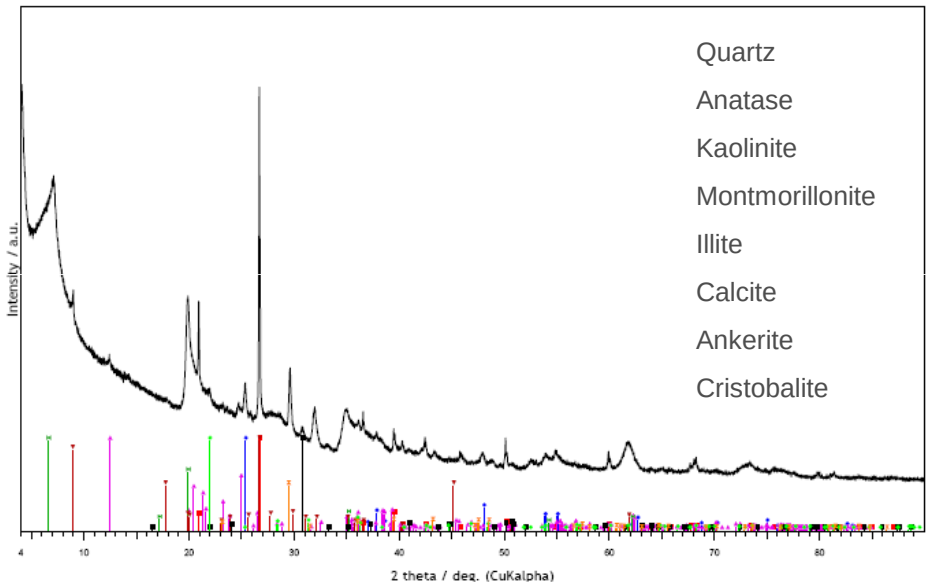
Purification of bentonite

- Comparison before and after purification (XRD, CEC)

Bentonite B75

before purification

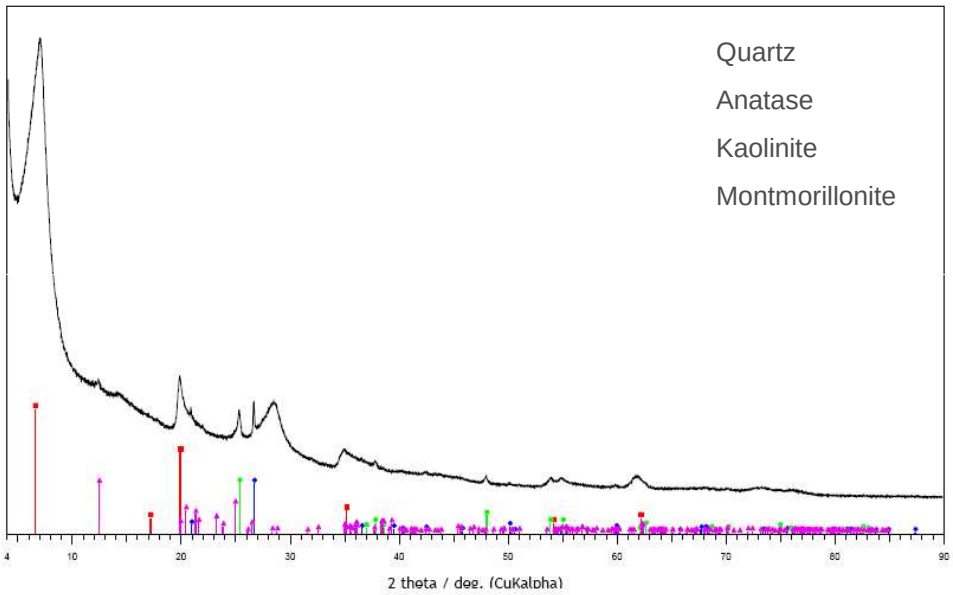
CEC 56.4 ± 0.7 meq/100g



Bentonite B75

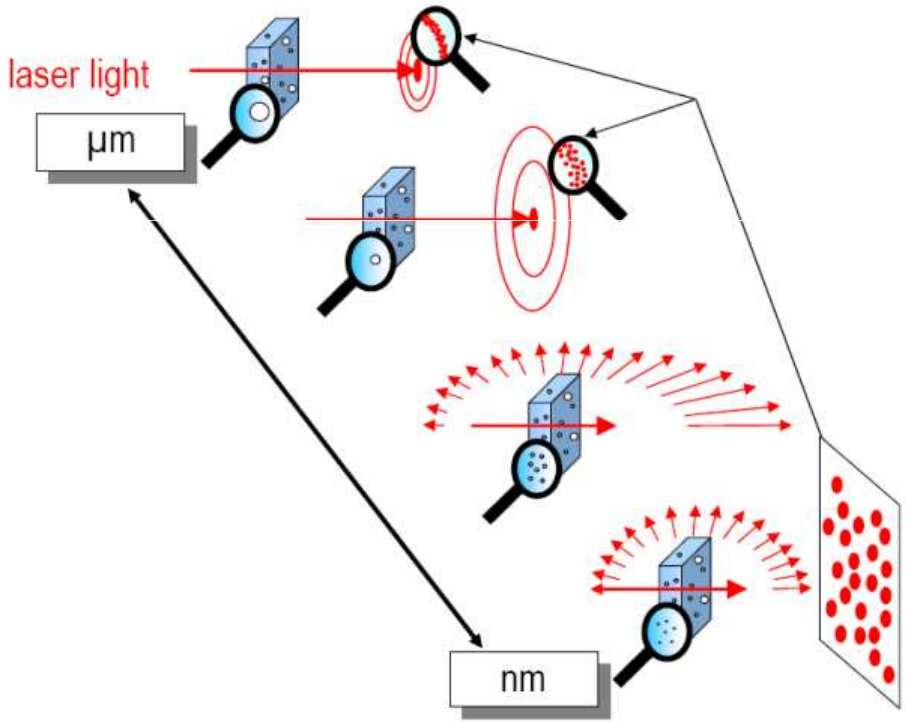
after purification, fraction < 2 μm, Na^+ form

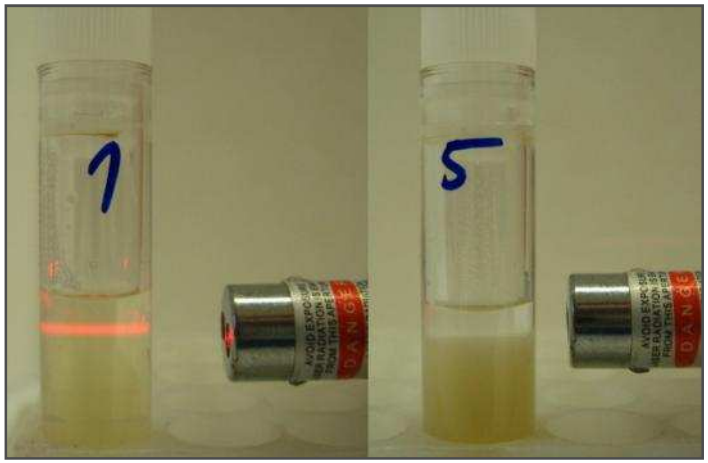
CEC 58.8 ± 2.43 meq/100g



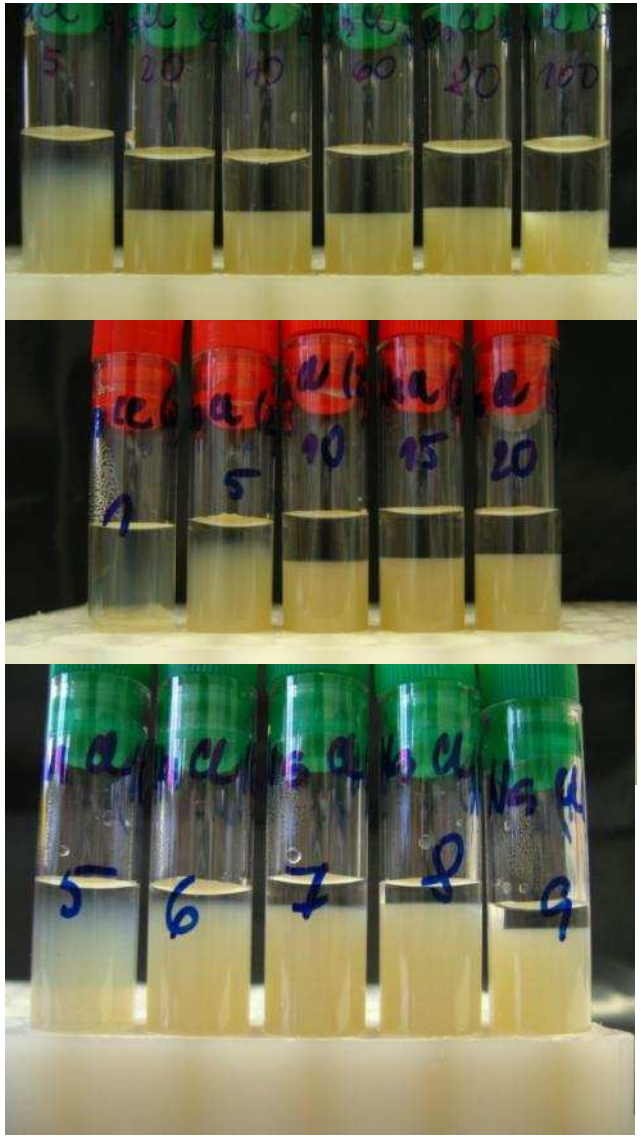
Coagulation of clay dispersions by inorganic cations (Na^+, K^+, Ca^{2+}, Mg^{2+})

- Series of test-tube tests
  - Determination of critical coagulation concentration (CCC) of univalent cations (Na^+, K^+) and divalent cations (Ca^{2+}, Mg^{2+}).
  - Bentonite B75 present in Na^+ as suspension in distilled water (0.5% w/w, pH = 7.3), particle size and distribution using PCCS (Mean hydrodynam. diameter 450 nm).
  - Different electrolyte (NaCl, KCl, $CaCl_2$ and $MgCl_2$) concentrations.
  - The visual inspection was performed after 30 minutes after the mixing, 24 hours after the re-mixing of the suspension and more than 48 hours and later with laser light beam.





Coagulation of clay dispersions by inorganic cations - NaCl



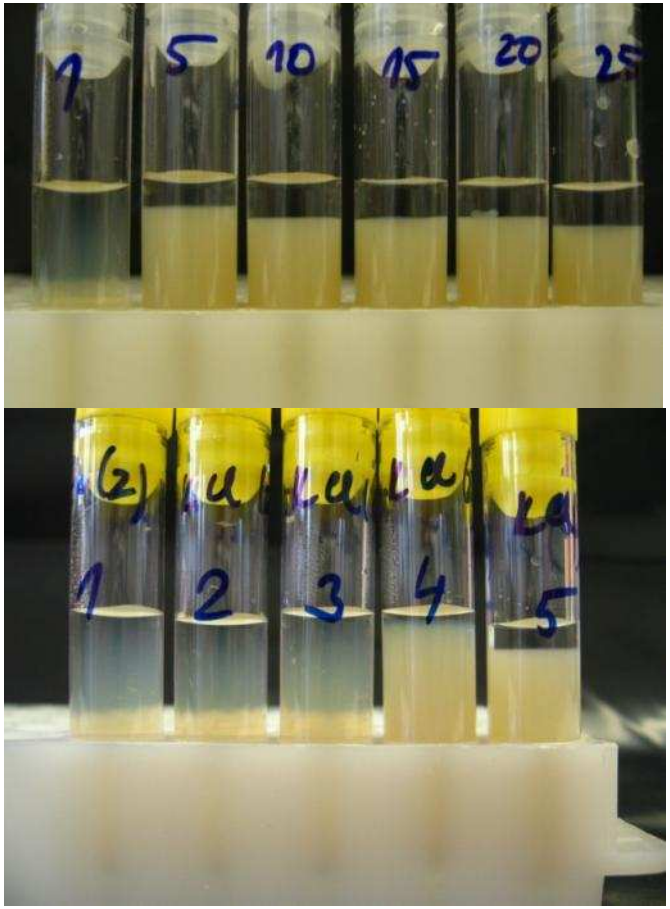
1) NaCl 5, 20, 40, 60, 80 and 100 mmol/l

2) NaCl 1, 5, 10, 15 and 20 mmol/l

3) NaCl 5, 6, 7, 8 and 9 mmol/l.

The CCC for the 0.5 % w/w bentonite suspension and NaCl solution was found to be in the range 6-7 mmol/l, which equals to the range 138-161 mg/l of Na.

Coagulation of clay dispersions by inorganic cations - KCl

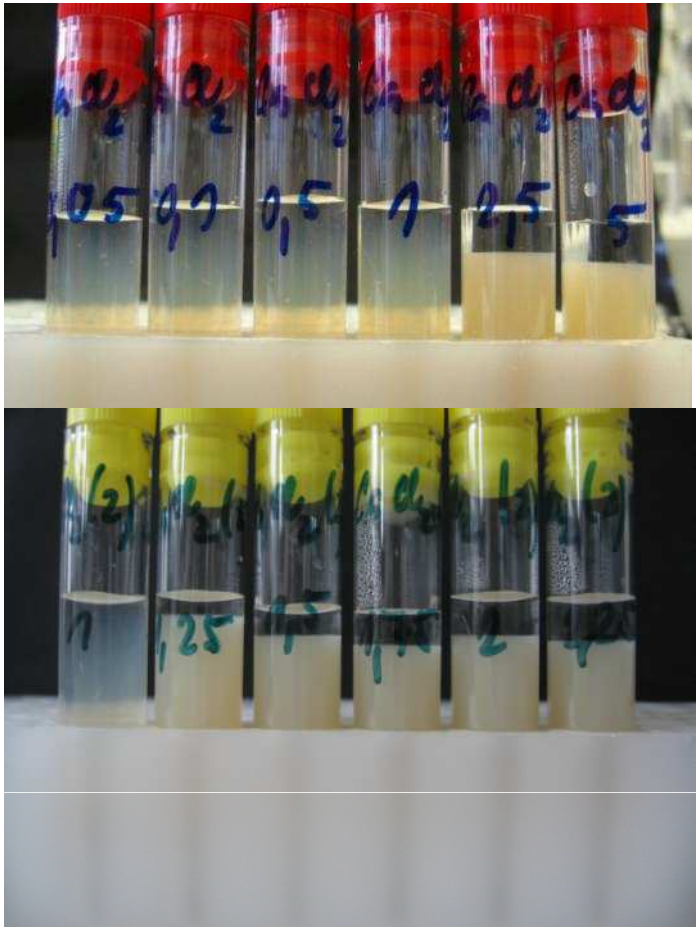


1) KCl 1, 5, 10, 15, 20 and 25 mmol/l

2) KCl 1, 2, 3, 4, 5 mmol/l

The CCC for the 0.5 % w/w bentonite suspension and KCl solution was found to be slightly shifted to lower concentrations and the CCC lies in the concentration interval 4-5 mmol/l KCl, which equals to the range 157-196 mg/l of K.

Coagulation of clay dispersions by inorganic cations - $CaCl_2$

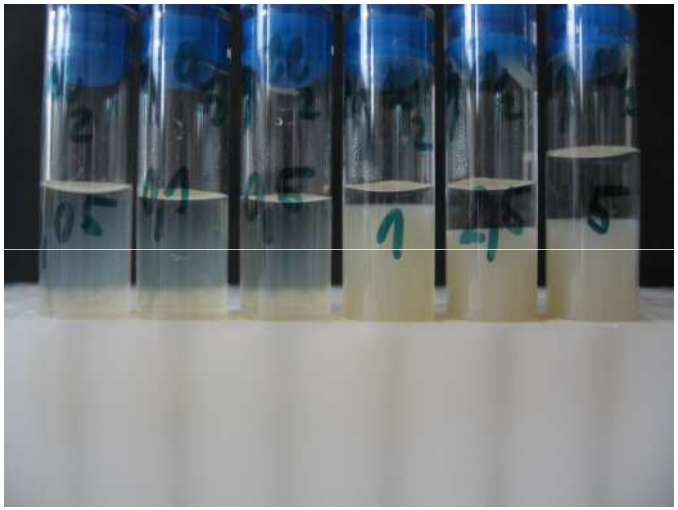


1) $CaCl_2$ 0.05, 0.1, 0.5, 1, 2.5 and 5 mmol/l

2) $CaCl_2$ 1, 1.25, 1.5, 1.75, 2 and 2.25 mmol/l

The CCC for the 0.5 % w/w bentonite suspension and $CaCl_2$ solution was found to be in the range 1-1.25 mmol/l, which equals to the range 40-50 mg/l of Ca.

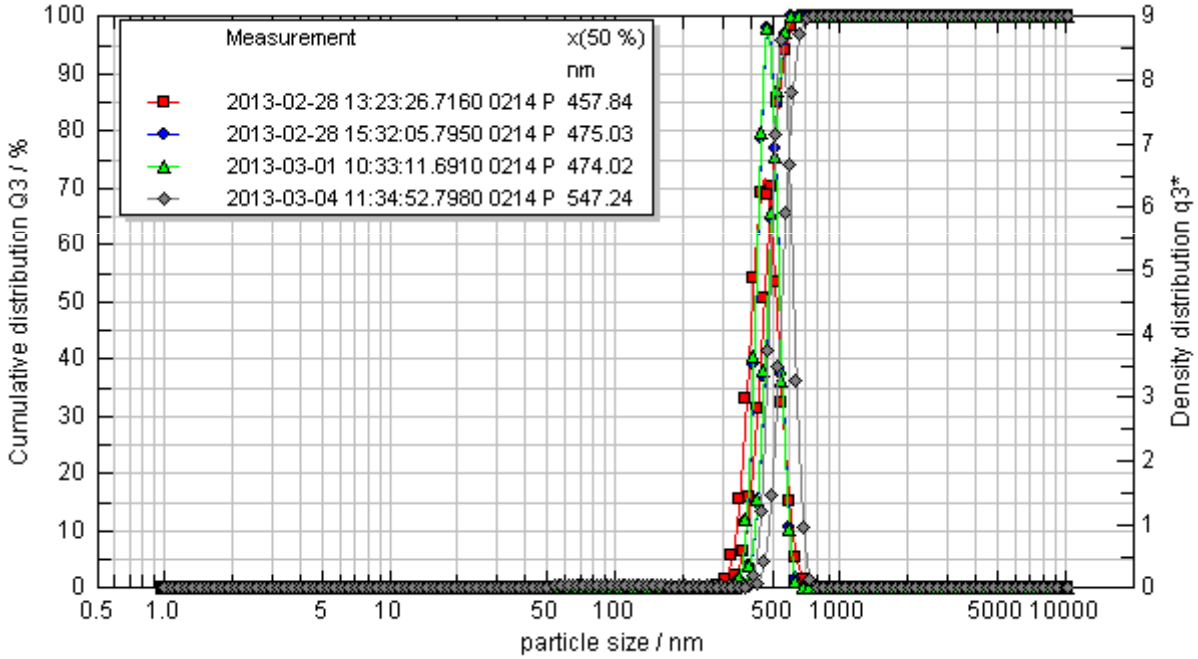
Coagulation of clay dispersions by inorganic cations - $MgCl_2$



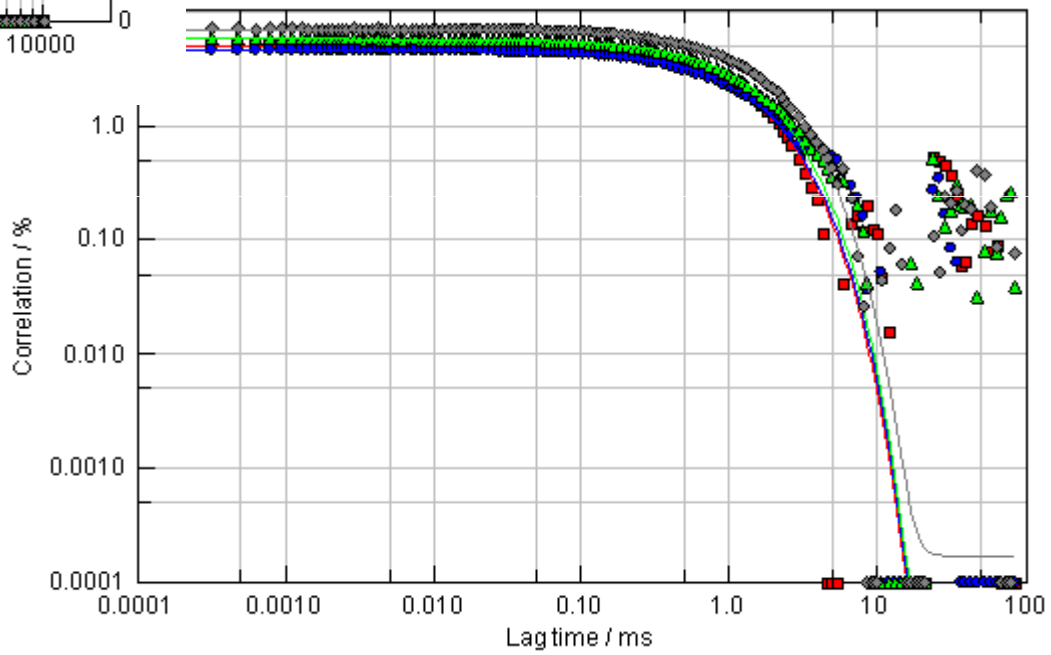
1) $MgCl_2$ 0.05, 0.1, **0.5**, **1**, 2.5 and 5 mmol/l

The CCC for the 0.5 % w/w bentonite suspension and $MgCl_2$ solution was found to be in the range 0.5-1 mmol/l, which equals to the range 12-24 mg/l of Mg.

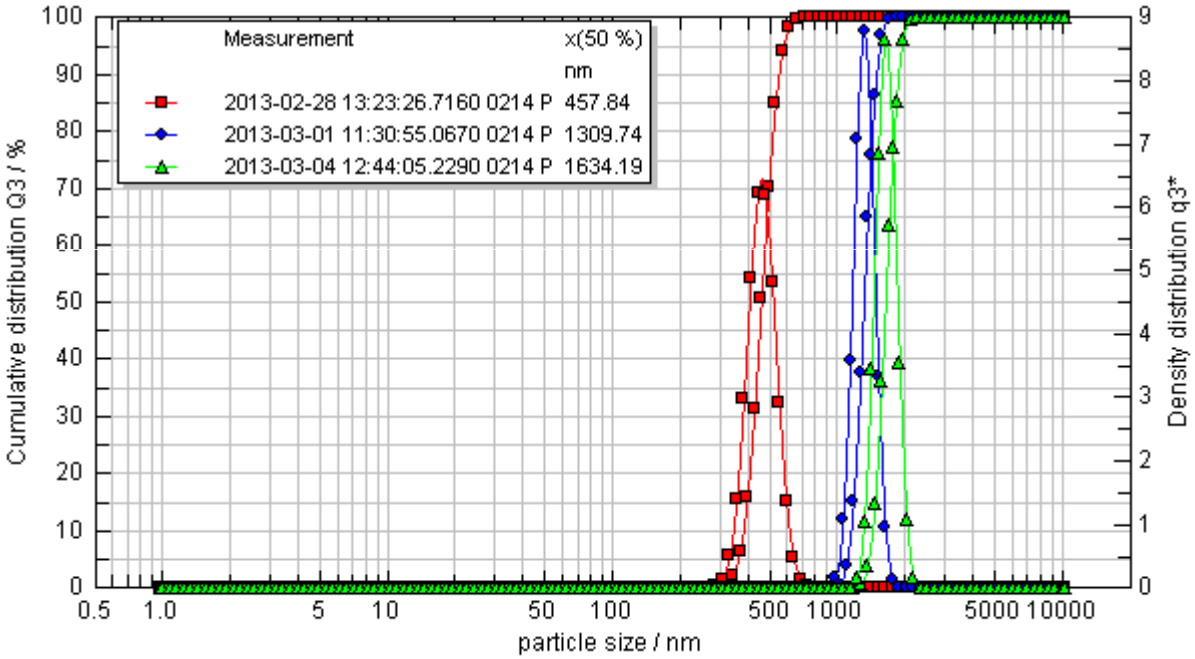
Coagulation of clay dispersions by inorganic cations - PCCS



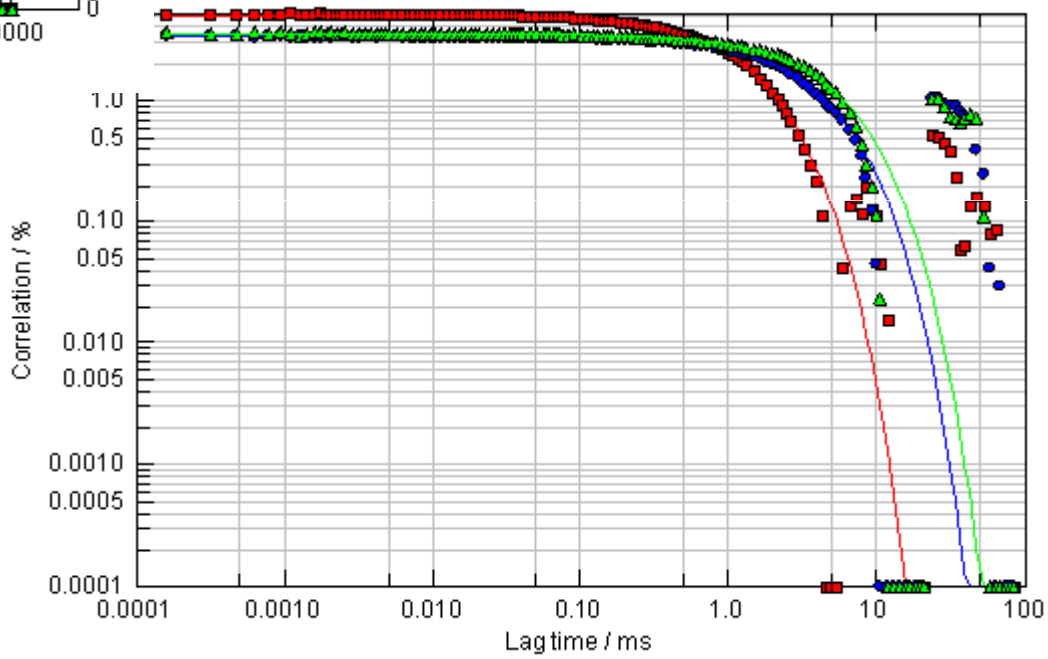
Bentonite B75 present in Na^+ form as suspension in distilled water (0.05% w/w) + 7 mmol/L NaCl



Coagulation of clay dispersions by inorganic cations - PCCS



Bentonite B75 present in Na^+ form as suspension in distilled water (0.05% w/w) + 100 mmol/L NaCl



Coagulation of clay dispersions by inorganic cations - summary

Comparison of obtained CCC values with appropriate concentrations in synthetic granitic water (SGW) representing ground water in granitic environment and liquid phase for further experiments.

Component	Concentration in SGW		CCC for selected cations	
	mg/l	mmol/l	mg/l	mmol/l
Na	10.642	0.463	138-161	6-7
K	1.8	0.046	157-196	4-5
Ca	27.001	0.674	40-50	1-1.25
Mg	6.405	0.264	12-24	0.5-1
F	0.2	0.011		
Cl	42.403	1.196		
SO_4	27.704	0.288		
HCO_3	30.412	0.498		
NO_3	6.3	0.102		

Conclusions

- Comparison of obtained CCC of selected uni and divalent cations for the 0.5% w/w suspension of B75 in simple electrolytes were found to be significantly higher than the concentrations of appropriate cations in the SGW. In the case of univalent cations, the observed CCC are more than one order of magnitude higher than the appropriate concentration in groundwater. In the case of calcium and magnesium, the CCC was found to be only approx. two times higher than the concentration in groundwater.
- This finding is important for future experimental work, because the concentration of Ca and Mg in the solution may be influenced by the presence of calcite and gypsum present in bentonite or rock material.
- It has to be noted here that presented results are valid for the purified B75 converted to sodium form and given suspension.

- Further experiments will focus on variations in coagulation experiments (w/w ratio of bentonite dispersions, materials: natural Rokle bentonite, MX-80) and on organic complexing agents (e.g. humic substances).
- PCCS measurements (coagulation vs. time).

- 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.