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Status report on the influence of complexing agents on clay colloid stability

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Starting point

Clay colloid stability is one of the key question for predicting their potential influence on the migration of radionuclides. This is greatly dependent of the geochemistry of the environmental medium and in particular of chemical parameters like the pH, the ionic strength, the ionic composition and the natural presence of (in-)organic complexing agents among with the humic substances (humic and fulvic acids).

Measurements on the influence of dissolved organic carbon (DOC) on clay colloid stability (Ca- and Na-CCC) are needed to reduce the uncertainty concerning the potential stabilizing effect of this kind of naturally occurring material.

The aim of this additional experimental work program is to examine in more details the effect of the addition of fulvic acids (FA) on the agglomeration process.

Coagulation of clay dispersions in presence of electrolyte and humic acids (ÚJV Řež, a. s.)

In granitic host rock (as considered for Czech concept of Deep Geologic Repository - DGR) the concentration of natural organic substances is generally low. The presence of organic substances is expected to be associated with microbial and anthropogenic activities and materials used in the construction of DGR. However the interaction between the clay colloids and organic molecules greatly influences the critical coagulation concentration (CCC) of clay particles and therefore we studied this phenomenon.

We aimed on the kinetics of coagulation of clay dispersion in presence of NaCl electrolyte and humic acids (HA). HA are natural organic substances often occurring in surface waters and near-surface groundwaters. The HA was extracted by alkaline method from organic rich sample, which stems from near-surface sediments (natural analogue Ruprechtov, for details see [1]). The clay suspension was prepared by mixing of purified Czech bentonite B75 and distilled water with initial concentration 100 mg/L.

Test-tube coagulation tests

First the critical coagulation concentration (CCC) of univalent cations (Na^+) in presence of HA were determined in the series of test-tube coagulation tests for one bentonite suspension concentration (0.005% w/w, i. e. 50 mg/L) and different NaCl electrolyte concentrations (10 to 500 mmol/L) and HA concentrations (0 to 2 mg/L of total organic carbon). The pH range varied from 5.9 to 6.7. The coagulation was tested according to the procedure described in [2]: 30 minutes after the mixing and 24 hours after the re-mixing of the suspension and more using visual inspection and laser light beam. Finally the presence/absence of particles in the upper part of dispersion was confirmed by photon cross correlation spectroscopy (PCCS) at Nanophox instrument (Sympatec GmbH, Germany). Figure 1 illustrates the obtained results.

The CCC for clay suspension in presence of NaCl electrolyte linearly increases with addition of HA. For higher concentration of HA the linear trend may not be valid as it is described in [3], where linearity is maintained for HA concentration up to 10 mg/L for Fe(III)-montmorillonite.

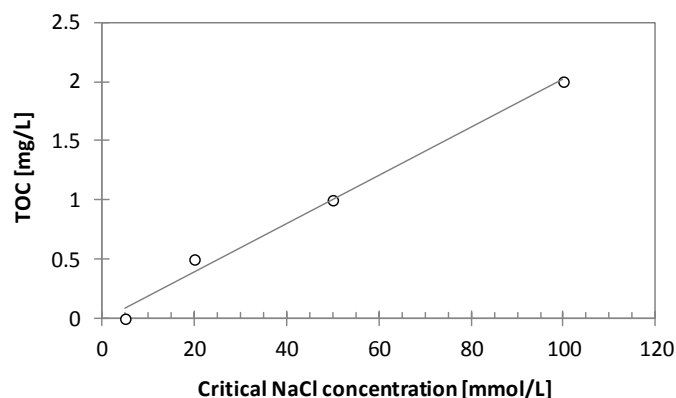


Figure 1. The CCC for clay suspension (0.005 % w/w) in presence of cation Na^+ (as electrolyte NaCl) linearly increases with addition of HA (expressed as total organic carbon - TOC).

Coagulation kinetics experiments

The coagulation kinetics of clay dispersion (0.005% w/w, i. e. 50 mg/L) in presence of NaCl electrolyte (10, 50 and 100 mmol/L) and HA (0 to 2 mg/L of total organic carbon) was studied by PCCS starting with well-dispersed system and following the increase in average hydrodynamic radius with time as the particles undergo coagulation. 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). For data evaluation the method of 2nd cumulant was used. The CCC for system only with NaCl electrolyte (without HA) was measured between 3-5 mmol/L (see Figure 2a). It is comparable with previous test-tube coagulation tests results. Below the CCC the mean hydrodynamic size do 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. For NaCl concentration > 10 mmol/L and experimental clay suspension the mean hydrodynamic size fluctuates in quite high range (see Figure 2c and 2d, open circles). The coagulation rate is probably so fast, that very large aggregates are created next to smaller one and this cause the high variations in the size.

The presence of HA significantly increases the colloidal stability of bentonite particles (Figure 2b-d), which also means, that in presence of HA the more concentrated NaCl electrolyte is needed for coagulation of clay dispersion (the CCC is higher). For example the CCC is four

times higher for system with 0.5 mg/L TOC than for system without HA. This effect seems to be primarily due to the reversal of edge surface charge from positive to negative, thereby preventing edge-to-face interactions. Very probably the HA is adsorbed on the clay edge surfaces due to the surface complexation between clay aluminol and HA carboxyl groups [4].

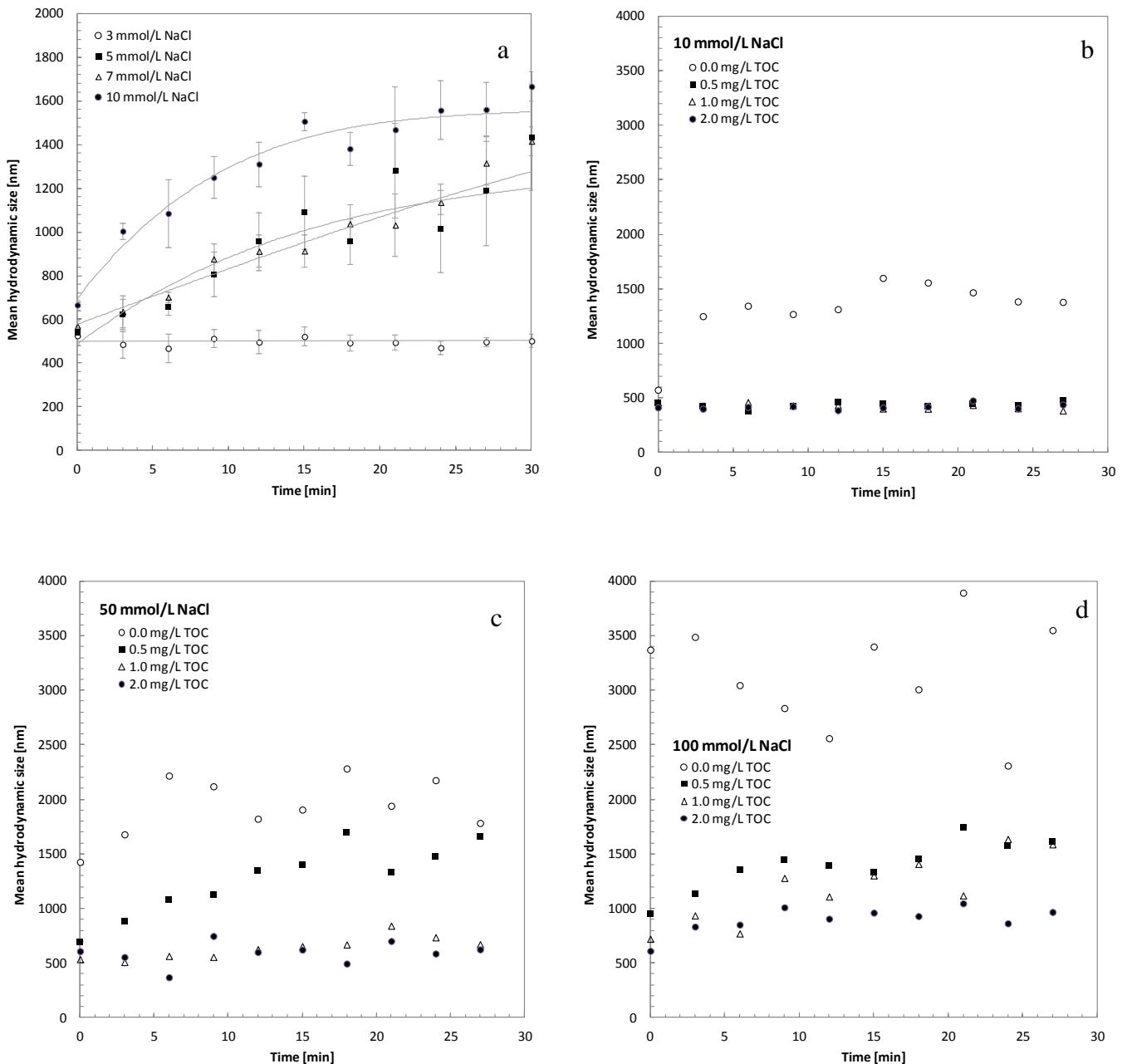


Figure 2. Coagulation kinetics of clay suspensions (0.005 wt. %) in presence of a) different concentration of NaCl electrolyte, points with 1σ error bars and trend, b) 10 mmol/L NaCl and different concentrations of HA referred as TOC, c) 50 mmol/L NaCl and different concentrations of HA referred as TOC, c) 100 mol/L NaCl and different concentrations of HA referred as TOC.

Influence of organic matter (fulvic acids) on the stability of clay colloids prepared under different chemical conditions (KIT-INE)

Experimental approach

Different clay colloidal stock suspensions have been used. These suspensions were prepared from a delaminated clay suspension (MX80, fraction <63 μm) prepared in 1 M LiCl and then centrifuged, rinsed and re-suspended 4 times in different electrolytes (see deliverable D4.5). The colloid concentration and resulting sizes obtained in each case are summarized Table 1.

Table 1. Colloid concentrations and sizes in each of the 6 clay colloidal stock suspensions, SGW = synthetic ground water, it contains Na^+ , Ca^{2+} , SO_4^{2-} , Cl^- , F, a trace amount of Si, and HCO_3^- for SGW at pH ~ 8.5 .

Electrolyte	[Colloids] 4 th supernatant	Size range nm (PCS)
MQ	1.95 g.L ⁻¹	270-300
NaCl 1.3 10 ⁻³ M	1.38 g.L ⁻¹	240-300
CaCl ₂ 0.433 10 ⁻³ M	1.56 g.L ⁻¹	
NaHCO ₃ 10 ⁻³ M	1.59 g.L ⁻¹	270-310
SGW pH ~ 8.5	0.92 g.L ⁻¹	290-350
SGW \sim pH 5	0.87 g.L ⁻¹	270-320

The fast coagulation rates are determined in presence or not of FA by using the Photon Correlation spectroscopy following the method described in literature [4,5].

According to the time needed for the preparation of all the clay colloidal suspension only preliminary work was investigated with the following inorganic cations: Na^+ , Ca^{2+} , Mg^{2+} . The IS selected were 0.05 M, 0.1 M, 1 M and 3 M. The colloid concentration is fixed at 10 mg/L before starting the destabilisation. At a first glance no stabilization induced by the presence of FA at high ionic strength is observed. Data treatment and experiment are in progress and will be examined in much more details.

Management

An undergraduate student (Mrs Y. Heyrich) has gained a first experience in a laboratory by preparing the different suspensions and by receiving an introduction to the different analytical techniques used (especially the Photon Correlation Spectroscopy, PCS) during her work (03/06/13-26/07/13).

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