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# Status report on the effects of various anions

Author(s):
**M. Hedström, Clay Technology AB**
**J. Gondolli, R. Červinka, ÚJV Řež, a. s.**

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2

# Introduction

Knowledge of the critical coagulation concentration (CCC) for various sodium montmorillonites is important for the safety assessment of repositories for spent nuclear fuel as it provides concentration limits for the onset of bentonite erosion by dilute groundwaters. Many investigations regarding the CCC are performed on very dilute montmorillonite suspensions (Hetzel and Doner, 1993; Lagaly and Ziesmer, 2003) although it is not necessarily such systems that are most relevant for the assessment of the performance of bentonite in a repository (Birgersson et al., 2009). The CCC of dilute suspensions would be more relevant for the situation when e.g. a river transport clay particles into an estuary where they may coagulate. However, in a repository for spent nuclear fuel, the bentonite has a considerably higher density (dry density ~1600 kg/m$^3$) and in order for erosion to be limited a gel (sometimes also called attractive gel) has to be formed at the interface between the swelling bentonite paste and the groundwater. Nevertheless CCC values determined for Na-montmorillonites using NaCl appear to be unchanged from the dilute suspension (~0.1% w/w) to denser systems 1% w/w (Birgersson et al., 2009; Hedström et al., 2011) and recent work shows that gels appear at the CCC for clay concentrations up to 4 to 6% w/w depending on clay origin (Hansen and Hedström, 2014). Still the notion that CCC determined for dilute suspensions is the relevant parameter for the gelling of montmorillonite at the swelling front comes with a caveat: The CCC for dilute suspensions seem more sensitive to pH, whereas pH has very small influence on the NaCl concentration required for gelling of denser systems that are relevant for repositories for spent nuclear fuel (Hetzel and Doner, 1991, Birgersson et al., 2009, Goh et al., 2011).

**Nature of gels**

Montmorillonite gels are formed when the clay platelets bind to each other and form a space-filling network. The force of attraction between clay platelets is of Coulombic nature, between negatively charged faces, due to the structural charge, and the edges that have a pH dependent positive charge density. Attractive van der Waals forces are of course always present but those play only a minor role, if any, for the gel formation.
There are two commonly used metaphors to describe the gel structure, either as house of cards or as band-like structures formed from clay platelets in an "overlapping coin" arrangement. The fact that the gels have yield strength suggests a cross-linked structure, and based on the fact that gels can be formed at concentrations as low as 0.1% w/w, Birgersson et al. (2009) proposed that the gels are branched chains of overlapping coins rather than a house-of-cards structure, which hardly could be space filling at such low particle concentrations. However, the actual structure is not known, only the edge(+)–face(-) attraction is certain.

**Exchange**

It was pointed out already by Kahn (1958) that "In the flocculation of sodium montmorillonite by polyvalent cations, ion exchange plays a dominant role". Still during fifty years following the observation by Kahn, measurements of e.g. CCC for Ca$^{2+}$ in Na-montmorillonite appear in the literature e.g, Lagaly and Ziesmer (2003), although such statements lack meaning. How to handle and quantify the influence of exchange on gelling has however finally been fully resolved and tested experimentally (Birgersson et al, 2009; 2011; Hedström and Karnland, 2011). In particular, if the Ca-Na exchange suggests that the clay layer-charge is compensated by Ca$^{2+}$ to an extent of above 90%, montmorillonite will flocculate independently of overall

ionic strength. A homoionic Ca-montmorillonite does not form a sol even in deionized water, thus the CCC for Ca-montmorillonite is not a meaningful quantity (alternatively it is zero) (Birgersson et al., 2009; Hedström et al., 2011). Therefore Ca-montmorillonite will not pose a problem concerning colloidal erosion in a repository for spent nuclear fuel.

Finally we like to point out that exchange is also present if one exposes a sodium-converted montmorillonite to monovalent salts with cations different from $Na^+$. The extent of exchange depends on the clay concentration as well as the salt concentration (Birgersson et al, 2009; 2011), which appear to be totally overlooked by e.g., Lagaly and Ziesmer (2003).

# Results from Clay Technology AB

In the results from Clay Technology AB, CCC is determined from the observation of the presence of a macroscopic gel.

## NaCl

The CCC for Wyoming Na-montmorillonite, Wy-Na (from MX80) was found to be 20-25 mM. For Milos Na-montmorillonite, Mi-Na (from Deponit CA-N) the CCC was found to be 10 mM and for Kutch Na-montmorillonite, Ku-Na (from Asha 505) CCC was determined to 5 mM (Birgersson et al., 2009). More recent tests, performed at a larger number of different NaCl concentrations, give the following CCC values: Wy-Na, 20 mM (up to 6% w/w); Mi-Na, 6-8 mM (up to 4% w/w) and for Ku-Na, ~4 mM (up to 4% w/w) (Hansen and Hedström, 2014).

## $Na_2SO_4$

This was only tested for Wy-Na at 0.5% w/w and gel was formed at concentrations of 5 and 15 mM but not at 1 mM. The corresponding ionic strengths are 15, 45 and 3 mM.

## $Na_4P_2O_7$

Pyrophosphate is the anion that has the largest influence on the formation of montmorillonite gels as the anions bind to the positive edge and thereby block the edge-face attraction.

The addition of 0.25% tetra sodium pyrophosphate to 0.5% w/w Wy-Na suspensions increased the CCC for NaCl by almost an order of magnitude (Birgersson et al., 2009). Similarly addition of pyrophosphate to an existing gel was found to lead to an almost instantaneous disintegration of the gel. These observations are completely in line with recent rheological measurements on bentonite slurries (7% w/w) where it was found that the addition of polyphosphates totally removed the yield strength over the pH range 5-10 and drastically reduced the yield strength below pH 4 (Goh et al. 2011). Without adding polyphosphate, the yield strength was significant ~30 Pa even at pH 10, which led the authors to draw the inevitable conclusion that: "The nature of the nature of the clay particle edge charge must still be positive at this high pH level". Birgersson et al. (2009) tested the influence of pH on the formation of Wy-Na gel and found that CCC remained at 25 mM NaCl up to the highest tested pH value of 9.1. Similarly, in erosion tests using artificial fractures erosion have not been observed for Wy-Na provided that the NaCl concentration is above 20-25 mM even at pH up to 10.

# Results from ÚJV Řež, a. s.

## *Coagulation of clay dispersions by selected cations and anions*

The previous results from basic coagulation experiments were summarized in deliverable D4.2 and the following work continued with the investigation of the bentonite colloids stability (purified Bentonite 75 present in sodium form denoted as B75-Na) in a presence of various cations/anions and OH$^-$ ions.

In the first case, the critical coagulation concentration (CCC) of univalent cations (Na$^+$, K$^+$), divalent cations (Ca$^{2+}$, Mg$^{2+}$) and selected anions (NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$) were determined in the series of test-tube coagulation tests for one bentonite suspension concentration and different electrolyte concentrations. The B75-Na suspension was prepared as a stock suspension 0.1% w/w in deionised water and target particle concentration (working suspension 0.01% w/w and final experimental suspension 50 mg/l of solid particles) were prepared by dilution in deionised water or electrolyte solution. The final particle concentration 50 mg/l was selected due to conditions of analytical determination of CCC (see later).

The main aim of performed experiments was to determine the CCC for appropriate electrolyte solution and compare the results with the measured concentrations of selected granitic groundwaters to decide whether bentonite colloids will be present in the groundwater or will be coagulated at given conditions.

In the second case, the effect of varying pH in alkaline solutions on CCC was tested for the suspension containing 500 mg/l of solid particles. The pH varied from approx 8 to approx 13 to simulate the effect of alkaline solution coming from the concrete barriers of the repository. The source of higher pH were NaOH and KOH, hence the effect of high Na and K concentrations in the solution have to be taken into consideration in CCC evaluation.

The coagulation was tested according the procedure described in Berg, 2010 – 30 minutes after the mixing, 24 hours after the re-mixing of the suspension and more than after 48 hours using visual inspection and laser light beam. It was concluded that the inspection after first 30 minutes cannot provide satisfactory results and also the inspection after 24 hours provide in some cases (lower electrolyte concentrations) unacceptable results. Thus the inspection was extended to longer times (after more than 48 hours and later). For the final series of concentrations covering the CCC value, the photon cross-correlation spectroscopy (PCCS) (Nanophox, Sympatec GmbH, Germany) was used to confirm the presence or absence of colloidal particles and to determine their approximate size.

**Na:**
For the NaCl, the CCC was found to be 5 mmol/l at the final pH of 6.3; for the NaNO$_3$, the CCC was found to be 6 mmol/l at the final pH of 6.0 and for the Na$_2$SO$_4$, the CCC was found to be 3 mmol/l at the final pH of 6.1. Very low concentrations of solid particles were identified for the electrolyte concentration 5 mmol/l (NaNO$_3$) and 2 mmol (Na$_2$SO$_4$), with mean particle size in the range 900-1000 nm. The mean particle size of colloidal particles under the CCC was found to be in the range 330-500 nm that suggests the CCC shifts with the time to the slightly lower values. With the time increasing, the bentonite particles may still coagulate at given conditions. For the Na$_3$PO$_4$ electrolyte, the coagulation (and CCC) was not found in the concentration range expected in the granitic groundwaters – this range was set to the values from 0.5 to 100 µmol/l according to the analyses of real groundwater samples and the bentonite leachates.

**Mg:**
For the $MgCl_2$, the CCC was found to be 0.5 mmol/l at the final pH of 6.7; for the $Mg(NO_3)_2$, the CCC was found to be 0.5 mmol/l at the final pH of 6.4 and for the $MgSO_4$, the CCC was found to be 0.5 mmol/l at the final pH of 6.1. In contrast to the sodium, for the lower selected concentration of magnesium (0.1 mmol/l, below the CCC) the particle concentration was significantly higher, with the mean particle size of colloidal particles in the range 470-500 nm.

**K and Ca:**
For both K and Ca, the coagulation tests were performed for the chloride salts only. For the KCl, the CCC was found to be 3 mmol/l at the final pH of 6.1; for the $CaCl_2$, the CCC was found to be 0.5 mmol/l at the final pH of 6.5. It was concluded that the CCC for potassium and calcium is similar as for sodium and magnesium.
It can be said that both sodium and potassium, and magnesium and calcium act in similar way during the coagulation process and in real systems (e.g. natural groundwater) their effect can be simplified to the effect of $M^{1+}$ (Na+K) or $M^{2+}$ (Ca+Mg) cations, where $M^{2+}$ are more effective in coagulation. The effect of different anions cannot be confirmed with certainty at given conditions. The groundwaters form the Bohemian Massif deep granitic environment are expected to be rich in Na and $HCO_3$; Ca (Mg), $SO_4$ and Cl are expected in significantly lower amounts (Rukavičková et al., 2009). The composition of the synthetic granitic groundwater (Tab. 1) equals the average composition of granitic groundwaters up to 200 m depth. As can be seen, its composition is different from the expected deep groundwater – higher amount of Ca than Na and high amount of $SO_4$ and Cl.

**Tab. 1: Comparison of obtained CCC values with appropriate concentrations in synthetic granitic water (SGW). The average CCC value for Na calculated based on coagulation test with NaCl, NaNO$_3$ and Na$_2$SO$_4$.**

| Component | Concentration in SGW | | CCC for selected cations |
|---|---|---|---|
| | 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 |
| F | 0.2 | 0.01 | |
| Cl | 42.4 | 1.2 | |
| $SO_4$ | 27.7 | 0.3 | |
| $HCO_3$ | 30.4 | 0.5 | |
| $NO_3$ | 6.3 | 0.1 | |

**The effect of alkaline solutions**
For both NaOH and KOH with varying initial concentrations, the coagulation tests were performed in the range of pH approx 8-13. It has to be noted that the varying pH cannot be separated from the varying concentration of both sodium and potassium in the test suspension in this type of experiment. Thus the effect of pH (the effect of $OH^-$ ions presence) may be suppressed by the coagulation effect of counter ions ($Na^+$ or $K^+$). As can be seen from Tab. 2, this has been observed in the coagulation tests – coagulation was observed only for the samples containing the amount of sodium or potassium above their CCC (the CCC for particle concentration 500 mg/l were found to be 6 and 5 mmol/l for Na and K). In the case where the sodium or potassium concentration in the suspension is below the CCC for Na or K,

coagulation was not observed, even after prolonged time. The rising pH (from approx 8 to 12) does not have any significant effect on particles coagulation at given conditions.

**Tab. 2: The effect of alkaline solutions (as NaOH and KOH) on coagulation of bentonite suspension with particle concentration 500 mg/l.**

| Hydroxide concentration (mmol/l) | Final pH measured in the suspension | | Coagulation after 24 hours | |
|---|---|---|---|---|
| | NaOH | KOH | NaOH | KOH |
| 50 | 12.5 | 12.7 | yes | Yes |
| 5 | 11.8 | 11.7 | no | No |
| 0.5 | 10.6 | 10.6 | no | No |
| 0.05 | 8.5 | 8.8 | no | No |
| 0.005 | 7.7 | 7.8 | no | No |

**The effect of synthetic groundwater**

For this test, the synthetic groundwater with composition listed in Tab. 1 was used as a simulation of interaction of bentonite colloids with real groundwater. Three different particle concentrations were tested – 500, 50 and 5 mg/l of purified B75-Na. The test-tube test with visual identification was accompanied by a photon cross-correlation spectroscopy measurement of the mean hydrodynamic size and counting rate. For this measurement, reference samples of particle concentration 50 and 5 mg/l were prepared in deionised water. The visual identification showed that after 24 hours there are no colloids in the SGW solution for all samples. The PCCS measurement confirmed the visual inspection, with exception that some great particles (with size above 1 μm) are present in solution in all samples. Their presence in measured solution may come from the sampling operations (solution transfer from the test-tube to the measuring cuvette), because some visible clay aggregates were found to be attached to the inner wall of test-tubes and also on the surface of the solution in the test-tubes. The second PCCS measurement was performed after 192 hours and different sampling technique was used. For all samples, no colloids were detected; the counting rate was near the detection limit of the analyzer. According to this measurement, and in comparison to the measurement after 24 hours, it can be said that the SGW solution is not suitable medium for the long-time presence of bentonite colloids. The concentration of $M^{2+}$ in SGW is two times higher than CCC determined for the $Ca^{2+}$ and $Mg^{2+}$ alone.

**Tab. 3: Coagulation in the synthetic groundwater (with composition listed in Tab. 1), three different particle concentrations used; pH of the experimental system 7.6±0.1. >1μm means that only limited amount of great particles were detected; ~ DL means that the counting rate was near the detection limit; N.A. means not available (at very low counting rate the size of the particles cannot be calculated).**

| B75-Na particle concentration | Mean hydrodynamic size (nm) | Average counting rate (kcps) | Mean hydrodynamic size (nm) | Average counting rate (kcps) |
|---|---|---|---|---|
| Reference samples | After 24 hours | | After 192 hours | |
| 50 mg/l | 455-456 | 2150-2252 | | |
| 5 mg/l | 514-572 | 228-301 | | |
| | | | | |
| Samples in SGW | | | | |
| 500 mg/l | >1μm | 37-74 | N.A. | ~ DL |
| 50 mg/l | >1μm | 60-82 | N.A. | ~ DL |
| 5 mg/l | >1μm | 88-121 | N.A. | ~ DL |

It has to be noted here that results presented so far are valid for the purified Bentonite 75 converted to sodium form. From previous experiments with particle concentrations 500 mg/l it can be concluded that CCC for Na, K, Ca and Mg are almost identical to CCC for particle concentration 50 mg/l. The particle concentration of bentonite colloids in real system may be lower than 50 mg/l – for example the particle concentration in groundwaters at the Ruprechtov natural analogue site (clay formation containing bentonites, kaolinite and other clay minerals) is in the range 0.1-1 mg/l (Bouby et al., 2006).

For the raw Bentonite 75 (as produced), the CCC determination is much more complicated by the presence of activation reagent (sodium carbonate) contamination. At the present time, the bentonite source for product Bentonite 75 is different from previous time (bentonite comes from the different deposit) and the product is still contaminated by the presence of activation reagent. Thus, the different product Bentonite and Montmorillonite (BaM) produced for the food industry was obtained from the producer. The CCC test will be performed for this bentonite colloids in natural form (without any purification, only particle separation). The preliminary coagulation tests in SGW for various particle concentrations show that the results are almost identical to the results of coagulation tests in SGW for B75-Na.

# Discussion and conclusions

The CCC of NaCl varies among Na-montmorillonites from different origins. The lowest CCC value of 4 mM was obtained for Ku-Na, whereas for Wy-Na the CCC is ~20 mM. In between falls B75-Na with 5 mM and Mi-Na that form gel at 6-8 mM. Why the CCC varies among different montmorillonites is not entirely explored. Possible candidates are differences in layer charge (CEC), layer-charge distributions, e.g., Hetzel and Doner (1993) find that tetrahedral charges may lead to lower CCC, and clay platelet morphology. Among the montmorillonites studied here, Ku-Na has the highest amount of tetrahedral charge (Karnland et al., 2006) and B75-Na the lowest CEC (61 meq/100g).

Changing anion has only minor effect on the CCC, provided that the anion does not directly influence the layer charge, as in the case of polyphosphates and to some extent $OH^-$. For B75-Na CCC for $NaNO_3$ was found to be 6 mM and for $Na_2SO_4$ 3 mM (ionic strength 9 mM). Similarly for Wy-Na the CCC of $Na_2SO_4$ is ~5 mM. Thus the CCC for any non-interacting 1:1 salt would serve as a good indicator when to expect the formation of a montmorillonite gel.

Tests on B75-Na were also performed by altering the cations. As pointed out in the introduction such tests must also be evaluated taking exchange into account. The CEC of B75-Na is 61 meq/100g, which gives a $Na^+$ concentration of 0.03 mM at a clay concentration of 50 mg/l. Clearly the ion exchange is complete at a KCl concentration of 3 mM where the CCC is found. Thus the CCC for B75-K (the potassium converted clay) is 3 mM KCl. Similarly, the experiments where $MgCl_2$ and $CaCl_2$ were added to the B75-Na suspensions lead to a complete ion exchange.

Exploring the influence of interacting anions may be of less direct practical significance for the safety assessment of a repository for spent nuclear fuel, but are of utmost importance for the understanding of the chemico-physical forces that hold gels together. The effect of polyphosphates on the gelling provide evidence that the gels are formed from edge(+)–face(-) attraction.

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