BELBaR D4.2

Protocol for rheological measurements within the BELBaR project

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1   Background and aim

Compacted bentonite with high montmorillonite content has been proposed as buffer material surrounding canisters containing spent nuclear fuel in several concepts for final repositories.

Montmorillonite, which is the main constituent in bentonite, has an exceptional affinity for water which results in the build-up of a swelling pressure when bentonite (with access to water) is placed in a confined volume. There may be fractures intersecting the deposition hole and at those fractures the bentonite is not restricted but can continue to swell until equilibrium or steady state is reached.

Apart from an understanding of the swelling process, knowledge of rheological properties of bentonite is of importance for the modelling and the prediction of the behaviour of a bentonite buffer during the operational time of a repository for spent nuclear fuel. The viscosity of bentonite/montmorillonite suspensions is a quantity needed to predict the velocity field outside a deposition hole where the seeping groundwater comes in contact with the extruded bentonite. The bentonite may also behave as a gel rather than a liquid, and knowledge of the yield strength will tell if such a gel can withstand the shearing forces from the seeping water.

The aim of the present protocol is to provide suggestions regarding what systems to study with regard to montmorillonite/bentonite volume fraction (or concentration), cation composition (in particular the Ca/Na content) and ionic strength of the water in equilibrium with the montmorillonite/bentonite. Bentonite may be highly thixotropic and it is found that the handling and preparation influence the outcome from rheological measurement (Börgesson & Fredriksson, 1990; Birgersson et al., 2009). It is therefore important to also consider these aspects when using rheological data for modelling.

How to actually perform the measurements or what equipment to use is not part of the aim of the present protocol. The experimentalists are in those aspects referred to the manuals of their respective equipments. However, regarding the experimental procedure, it would be beneficial to perform the measurements at more than one temperature. One should also note the temperature before and after the experiment as energy is continually dissipated and may lead to an increase in temperature (Goodwin & Hughes, 2000).

A viscometer (e.g. Brookfield) would in most cases be sufficient to answer questions regarding viscosity or yield strength (Birgersson et al., 2009) that would enter basic models for erosion, but a rheometer (e.g. Bohlin or Physica) could bring additional understanding concerning viscoelastic properties (structure breakdown and build-up) (Börgesson & Fredriksson, 1990) although models for erosion may not need that level of detailed information (Liu & Neretnieks, 2006).

2   Montmorillonite phase/state diagram

The phase or state diagram for Na-montmorillonite is a convenient starting point for introducing the factors needed to take into consideration when deciding what systems rheology is warranted for. Figure 1 shows the schematic state/phase diagram for Na-montmorillonite. In the literature one can nowadays find a flora of exotic phases that would be subdivisions to the ones depicted in Figure 1, which follows the conventional terminology that can be found in e.g. Abend & Lagaly (2000). From a colloidal point of view a sol is a liquid phase, which in this case consists of clay particles (in the case of Na-montmorillonite the clay is possibly totally exfoliated) dispersed in low concentration NaCl aqueous solution. For low clay concentration (up to ~5g/l) the sol can be characterized as a Newtonian liquid
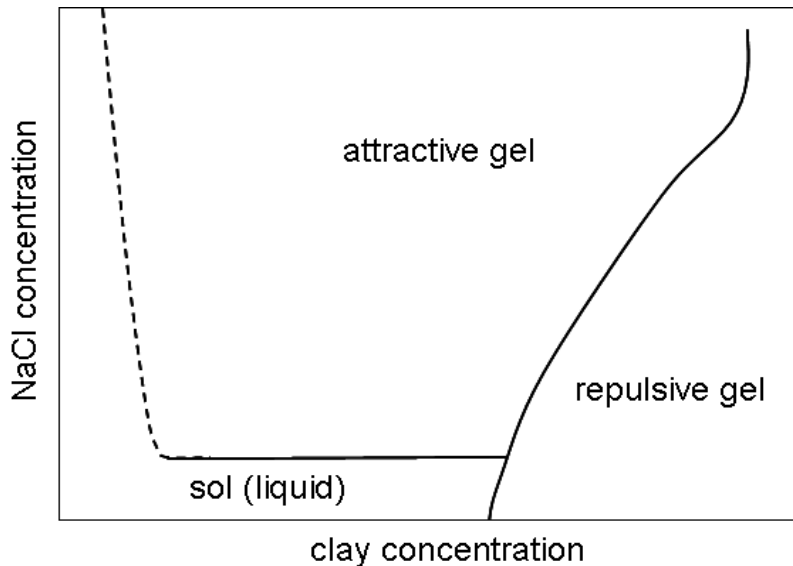
Figure 1 Schematic phase/state diagram for Na-montmorillonite.

but with increasing clay concentration the sol becomes more and more non-Newtonian as particle-particle interaction starts to influence the behaviour (Baravian et al., 2003; Birgersson et al., 2009). Under certain conditions it is also possible to obtain a phase separation under gravity into a virtually clay-free supernatant and a thick liquid containing all the clay particles at the bottom. Such exotic phase with strongly interacting clay particles should also be termed sol although such liquid is quite different from the dilute sol which is more akin to a gas. In the colloid literature one often see the distinction between liquid and gas, but the colloidal phase in both cases is liquid with dispersed solid particles and therefore should formally be termed sol.

When the clay concentration is higher than about 20-40g/l (the value depends on the sensitivity of the method) the clay is a repulsive gel provided that the NaCl concentration is low enough to not cause coagulation. Michot et al. (2004) find the value to be close to 20g/l for Wyoming Na-montmorillonite. In our laboratory we have taken a pragmatic view in defining the repulsive gel (Birgersson et al. 2009). A repulsive gel is a gel that would expand, provided that it has access to additional aqueous solution and volume. This is a situation that could be envisaged for the repository, where compacted bentonite may swell into water-bearing fractures. If the ionic strength of the water is sufficiently low, the expanding repulsive gel would eventually turn in to a sol. Therefore, the rheology of the repulsive gel/sol equilibrium (we assume here that there must exist an equilibrium between the repulsive gel and sol) is of particular interest for the colloid erosion scenario. A repulsive gel would naturally also have a swelling pressure and Michot et al. (2004) find the 20-g/l-gel to have a swelling pressure of about 4-500 Pa.

We also take a pragmatic view in defining the attractive gel, simply as a gel that does not expand if given access to excess aqueous solution. The attractive gel is found above the sol and to the left of the repulsive gel in the phase diagram in Figure 1. This means that the NaCl concentration must be higher than a critical value at which the system coagulates. Also a too dense system does not form an attractive gel since dense clay has a swelling pressure and therefore expands. In the laboratory it is possible to prepare attractive gels at very low clay concentrations 1-2g/l. Such attractive gels are very brittle and have very low yield strengths and hard to investigate with the standard Brookfield viscometer. On the other hand those extremely dilute attractive gels are unlikely to have any importance for the buffer evolution in

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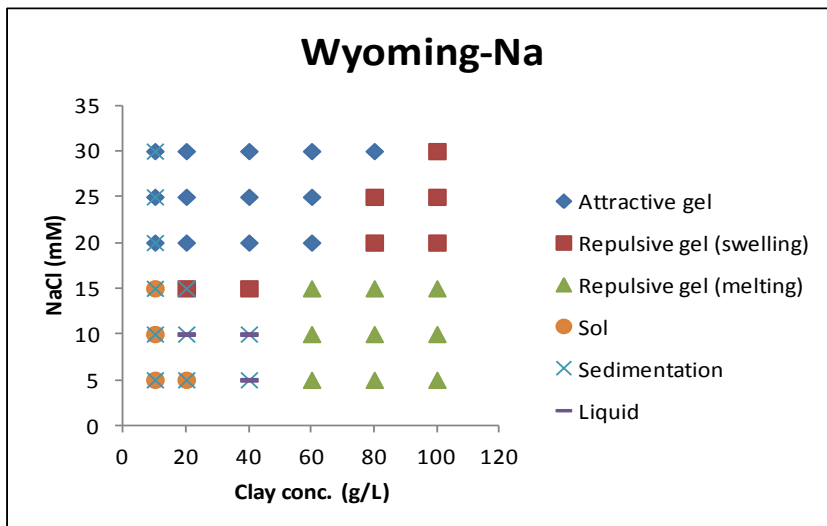
Figure 2 Measured phase/state diagram for Wy-Na montmorillonite. In this phase diagram the dense sol is termed liquid. Furthermore it is indicated where gravity has given rise to clear sedimentation, for example the attractive gels at 10 g/l are not formed fast enough, alternatively not strong enough to prevent some sedimentation of clay (Hansen & Hedström, 2013).

the repository. On the other hand, if a repulsive gel swell into an aqueous solution of sufficient ionic strength it would eventually turn into an attractive gel, which is represented by the line (border) separating the two types of gels to the right in Figure 1. Gels at this border have considerable yield strengths and are of course of high interest for rheological investigations.

The phase diagram for mixed Ca/Na-montmorillonite would in principle look the same as the one in Figure 1, provided that the equivalent charge fraction of Ca^{2+} in the clay is below 0.9 ($X_{Ca} < 0.9$). Clays with $X_{Ca} \geq 0.9$ behave similar to homoionic Ca-montmorillonite where the sol phase is virtually absent (See also Appendix 1). Furthermore colloidal erosion has not been observed for Ca-montmorillonite even when contacted with deionized water (Hedström et al., 2011).

3   Rheology for Na-montmorillonite

Figure 2 shows the experimentally determined (based on visual inspections) state/phase diagram for Wyoming Na-montmorillonite (Wy-Na). The montmorillonite is the 0.5 μm fraction from MX-80 Bentonite, and is turned into homoionic sodium form through repeated washings in 1 M NaCl. The excess NaCl is finally removed through dialysis.

This phase diagram gives rather clear indications which systems ought to be the focus for the rheological investigations. Above 20 mM NaCl the system is an attractive gel, which suggests that viscosity of the sol is only meaningful to determine for NaCl concentrations below 20 mM. If the NaCl concentration in the seeping water is above 20 mM, either in a repository or in an experiment simulating swelling into a fracture, the phase diagram imply that an attractive gel will be formed at the swelling front with a clay concentration of around 60 g clay per liter. Erosion experiments either in swelling-pressure test cells (Hedström et al., 2011) or in artificial-fracture systems have confirmed that no erosion takes place for Wy-Na montmorillonite provided that the NaCl concentration is above 20 mM.

In rheological measurements the repulsive gel to sol transition is found at about 20 g clay per liter for Wyoming montmorillonite (Abend & Lagaly, 2000; Baravian et al., 2003; Michot et al., 2004). In the phase diagram above we also find repulsive gel at about 20 g/l at NaCl concentration of 15 mM. Below 15 mM the

test-tube experiments used to determine the phase diagram in Figure 2 gave a sol. This is not a severe discrepancy, but suggests that the repulsive gel to sol transition is better determined using rheological methods. The findings by the above mentioned authors could be confirmed by rheological experiments within BELBaR.

Na-montmorillonites from other origins, for example Milos, Greece and Kutch, India, form attractive gels at lower NaCl concentrations (Birgersson et al., 2009; Hansen & Hedström, 2013). However the repulsive gel to sol transition is found to occur at similar clay concentration which again suggest that in the rheological measurements within BELBaR should scan the range form 15 to 40 g clay per liter in search for this transition.

The role of edge-face interactions, which is the mechanism giving attractive gels, could also be addressed using rheology by studying yield stress and viscosity of Na-montmorillonite in NaCl solution with and without the addition of tetrasodium pyrophosphate. Unfortunately this technique cannot be used for calcium-containing systems because calcium pyrophosphate precipitates.

4   Rheology for mixed Ca/Na montmorillonite

Apart form tests using bentonite, e.g., MX-80 (Birgersson et al., 2009) which naturally contains a mix of mono- and divalent counterions, tests on mixed Ca/Na-montmorillonite with controlled Ca/Na ratio is still un unchartered territory. In the repository the clay will contain a mixture of both mono- and divalent cations and the proportion between the two types will vary over time depending on the time variations of ionic composition of the groundwater. This fact and the finding that aqueous solutions containing 2-4 mEq/l positive charges prevent erosion of mixed Ca/Na-montmorillonite in swelling pressure cell set-up (Birgersson et al., 2009) make the mixed Ca/Na system the most relevant for the assessment of possible erosion during the operational time of the repository.

In Birgersson et al., (2009) the clay was in equilibrium with a low ionic strength aqueous solution (2-4 mEq/l positive charge) which effectively mean that the NaCl concentration was 2-4 mM and the $CaCl_2$ concentration in the low µM range in accordance with the exchange equilibrium for montmorillonite (Karnland et al., 2011). Non-equilibrium, artificial fracture tests (1 mm aperture) with flowing NaCl solutions hints slightly higher ionic strengths to prevent erosion (Schatz et al., 2012). For the rheological investigations of the attractive gels these findings suggest that being in proper exchange equilibrium is important and sample preparation in e.g. dialysis tubes or rigid cells with dialysis filters could be a possible way to achieve this.

Without having a full phase diagram (like the one in Figure 2) at hand for mixed Ca/Na-montmorillonite it is difficult to give specific recommendations what clay concentrations to focus the investigation on. The precise systems and ionic strengths can only be decided based interaction among the groups doing rheology and the groups doing erosion tests and/or phase diagram determinations within the BELBaR project. Most likely though, the sol to repulsive gel transition will occur in the range 15-40 g clay per liter, possibly at the higher values as the osmotic pressure will be lower, the higher the calcium content in the clay. Based on earlier studies the repulsive gel will also form at lower ionic strength than for the corresponding homoionic Na-montmorillonite.

Finally a reminder that rheology on homoionic Ca-montmorillonite is difficult and may also lead to misleading results because at least dilute suspensions phase separate quickly to supernatant and grains of Ca-montmorillonite on the bottom of the vessel. In such cases what is measured is basically the viscosity of the supernatant (Birgersson et al., 2009). This difficulty is connected to the observation that Ca-montmorillonite does not exfoliate and form a sol. On the other hand this also means that Ca-montmorillonite does not pose a problem regarding erosion. With respect to exfoliation, Figure 3 in Appendix 1 shows that mixed Ca/Na-montmorillonite behaves similarly to homoionic Na-montmorillonite

and presumably exfoliate completely up an equivalent charge fraction $X_{Ca} = 0.6$. Based on the results in Figure 3, the problems with rheology measurements on homoionic Ca-montmorillonite will not be encountered for $X_{Ca} < 0.8$. In order to limit the number of rheological investigations for the mixed systems, $X_{Ca} = 0.25$, 0.5 and 0.75 ought to be sufficient and give a representative picture.

5 Possible tests on bentonite

These tests will be conducted at Clay Technology AB and will focus on yield stress measurements using vane. The rheological properties will be correlated to the ionic strength, which in the case of bentonite will be governed by the amount of soluble accessory minerals. A given amount of bentonite in a given amount of deionized water will set the boundary conditions. To capture the conditions relevant for the erosion scenario bentonite will be placed at the bottom of a container and be allowed to swell freely in deionized water. As long the ionic strength (ion composition) is above the limit where an attractive gel is formed there will be a phase separation in the system and the rheological properties will be measured in the bentonite gel at the bottom of the container. Preparatory tests with this setup and methodology have already been carried out at a vane rotation rate of 0.1 rpm.

w_r	amount clay/l water [g/l]	Nominal Na_2SO_4 conc. [mM]
30	33.3	1.4
40	25.0	1.0
50	20.0	0.8
100	10.0	0.4
200	5.0	0.2

Table 1 Proposed test matrix for MX-80 gels. The water to solid mass ratio w_r is the average ratio and not the water to solid mass ratio of the attractive gel phase. The nominal Na_2SO_4 concentration is calculated from a gypsum content of 0.7% in the dry clay.

Input parameters are total mass of clay, total amount of deionized water and swelling/resting time before measurement.

Measured properties are pH, Na and Ca concentrations in supernatant (for MX-80 the ionic strength will essentially be governed by Na_2SO_4), yield stress, average water ratio of the bentonite gel phase (supernatant decanted), and content of solids in supernatant.

Table 1 shows the proposed test matrix for MX-80. Similar number of tests could be performed for the bentonites for Asha 505 and FEBEX.

The rheological properties of clay are path dependent. It was earlier found (Birgersson et al., 2009) that the rheological response was different in systems where the clay was initially mixed in NaCl solution compared to the case where clay first was dispersed in deionized water prior to the addition of NaCl. In the present study we aim to let the montmorillonite swell freely in the electrolyte as this situation more closely resembles the actual scenario in the repository.

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Appendix 1: Behaviour of mixed Ca/Na-montmorillonite based on turbidity measurements
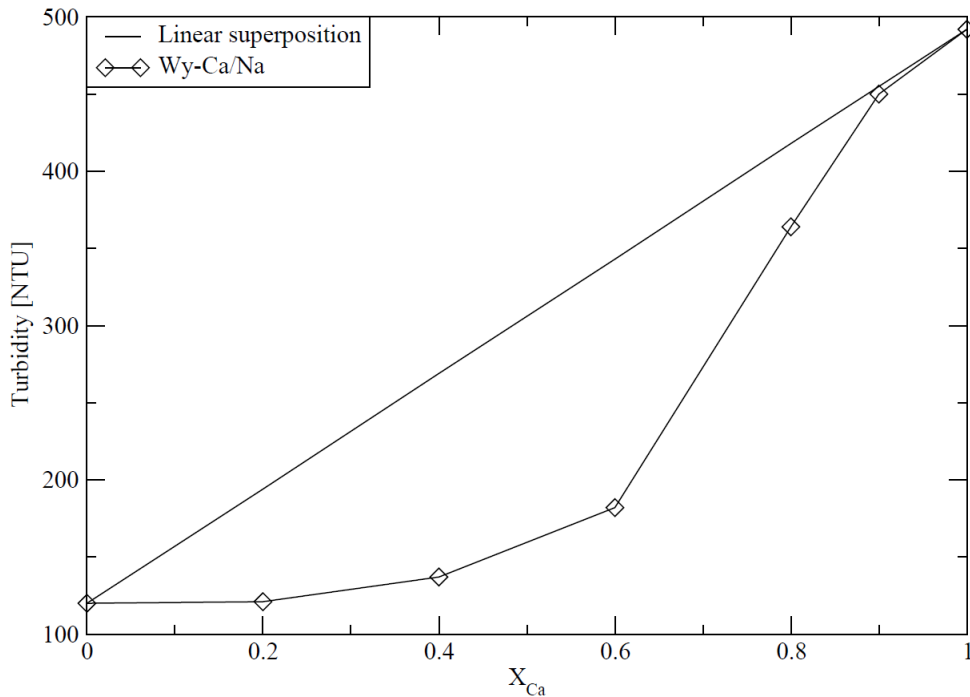
***Figure 3** The turbidity dependence of Ca/Na-montmorillonite suspensions (1g/l) on the fraction of exchangeable Ca. The straight line represents a linear superposition of the turbidities for Na- and Ca-montmorillonite (see text) (Hedström & Birgersson, 2013).*

From theory we know that turbidity of a solution is proportional to the particle concentration. However turbidity is also proportional to V_p^2 where V_p is the volume of the scattering particle. Thus the fact that turbidity of a Ca-montmorillonite suspension is higher than the turbidity of a Na- montmorillonite suspension of the same concentration (weight montmorillonite/volume water) indicates that Na-montmorillonite separate into smaller particles than Ca-montmorillonite.

Figure 3 shows the final (stabilized) turbidity response of mixed Wy-Ca/Na montmorillonite as a function of the fraction of Ca^{2+} in the clay. Starting material are suspensions of homoionic Wy-Ca and Wy-Na montmorillonite at a concentration of 1g/l. The turbidity of the suspensions of the homoionic clays are 490 and 120 NTU for Wy-Ca and Wy-Na respectively. A mixed suspension of volume V with calcium fraction X_{Ca} is obtained by mixing $X_{Ca} \cdot V + (1 - X_{Ca}) \cdot V$. If the two types of clay were unaffected by the mixing then the expected turbidity of the mixed suspension would be a linear superposition, i.e. $\mathrm{Turb}(X_{Ca}) = X_{Ca} \cdot \mathrm{Turb}(\mathrm{Ca}) + (1 - X_{Ca}) \cdot \mathrm{Turb}(\mathrm{Na})$ as illustrated in Figure 3. However, the measured turbidities show large non-linearity and lie below the linear response. For $X_{Ca} \leq 0.6$ the turbidity is close to that of homoionic Wy-Na showing that the particle size (sometimes called "tactoid" size) of Wy-Ca/Na does not differ significantly from homoionic Wy-Na. Evidently by just mixing Ca-montmorillonite with Na-montmorillonite the "tactoids" that are present in Wy-Ca break-up. One could envisage that at high Ca fractions the mixing process could work in the opposite direction so the mixed montmorillonite would behave more like Wy-Ca. In that case the measured turbidity would lie above the

linear superposition line. From Figure 3 we see instead that Turb($X_{Ca} = 0.9$) lie close to the superposition line and Turb($X_{Ca} = 0.8$) clearly falls below. Still the higher turbidity of the clay with $X_{Ca} = 0.8$ compared to homoionic Wy-Na indicates incomplete delamination or dispersion, which is also in accord with the observation of the 19 Å diffraction peak also at low dry densities (SAXS measurements at MAX-lab by D. Svensson and S. Hansen).