

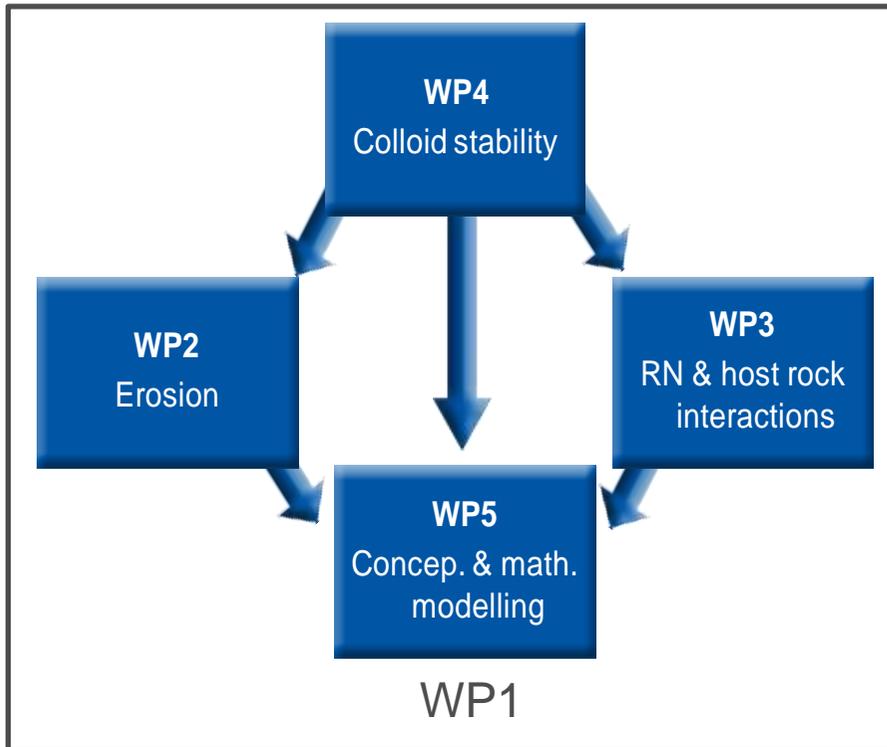
BELBaR Project

Colloid formation and stability Summary of results from WP4

(CIEMAT, KIT-INE, ClayTech, KTH, B+TECH, SKB, ÚJV)

Edited by Radek Červinka
ÚJV Řež, a. s., 2016

WP4: Objectives



- 1) **Clay colloid stability studies under different geochemical conditions with respect to ionic strength and pH**

Reason for different behaviour of different clays - trend or correlation between the bentonites characteristics and its stability

- 2) **Critical coagulation concentration, coagulation kinetics, (ir)reversibility of coagulation process**

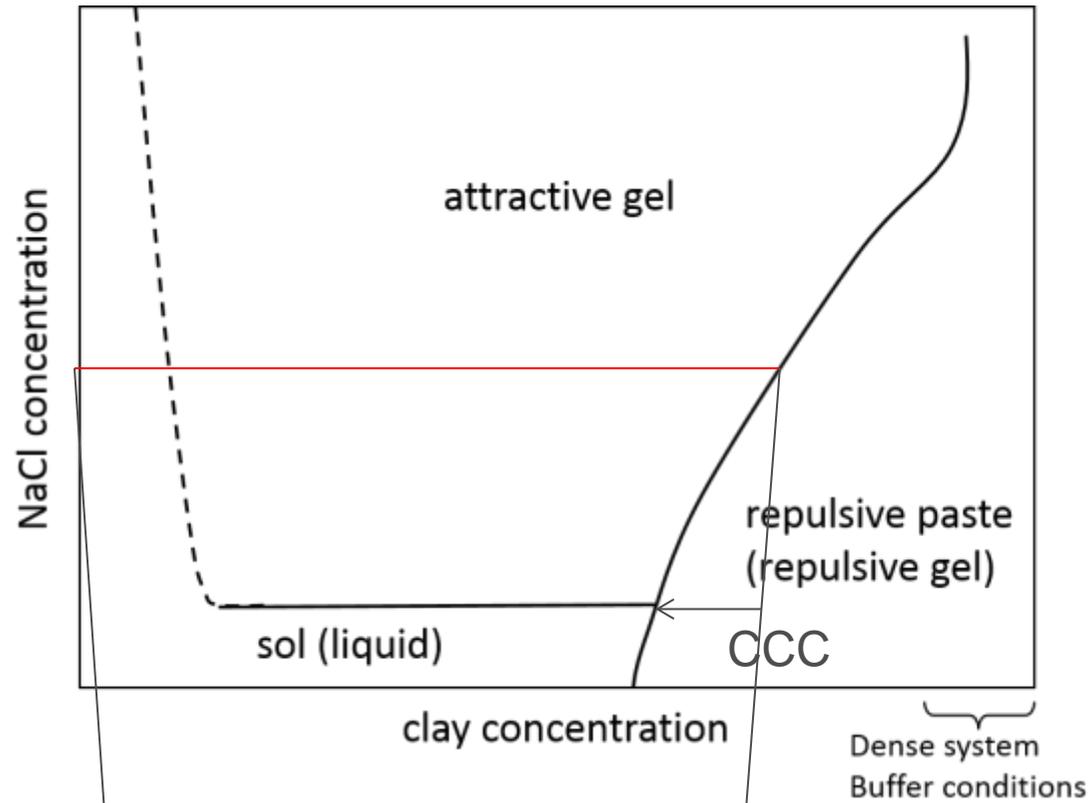
If we are at the boundary, close to conditions which are favourable for clay colloids coagulation, the aggregation process can be very slow.

If the hysteresis of coagulation process take a place, the aggregation or disaggregation of clay colloid will not undergo in the same dimensions.

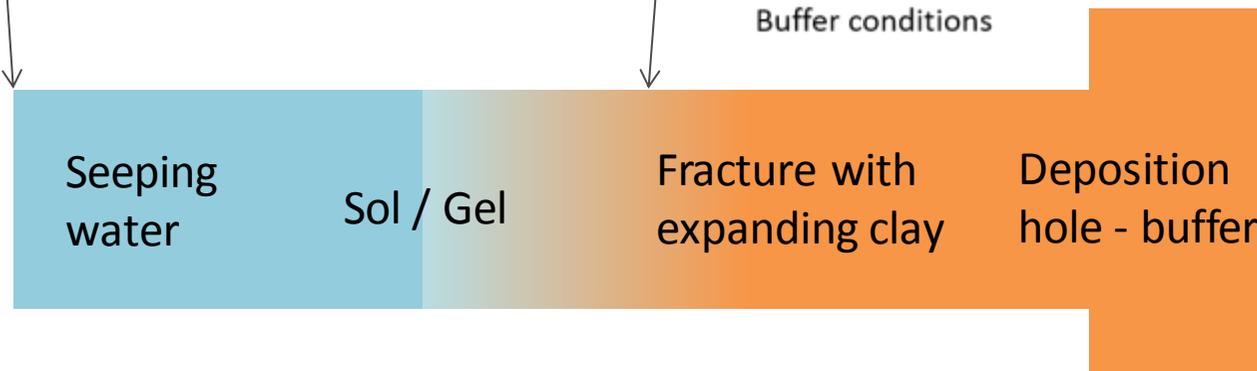
- 3) **Role of complexing agents (organic / humic substances) on clay colloid stability**

Interaction between the clay colloids and organic molecules greatly influences its stability

WP4: Phase (state) diagram of Na-montmorillonite



The investigations suggest that, provided the ionic strength of the ground water is above the CCC, the highly compacted clay in engineered barriers will act as a swelling repulsive paste and expand. Once the lowest clay concentration at the swelling front is below the clay concentration required for paste formation, the clay will form a gel. The lowest limit appears to be about 60 g/l, although it can be higher depending on the type of montmorillonite as well as the salinity in the surrounding system.



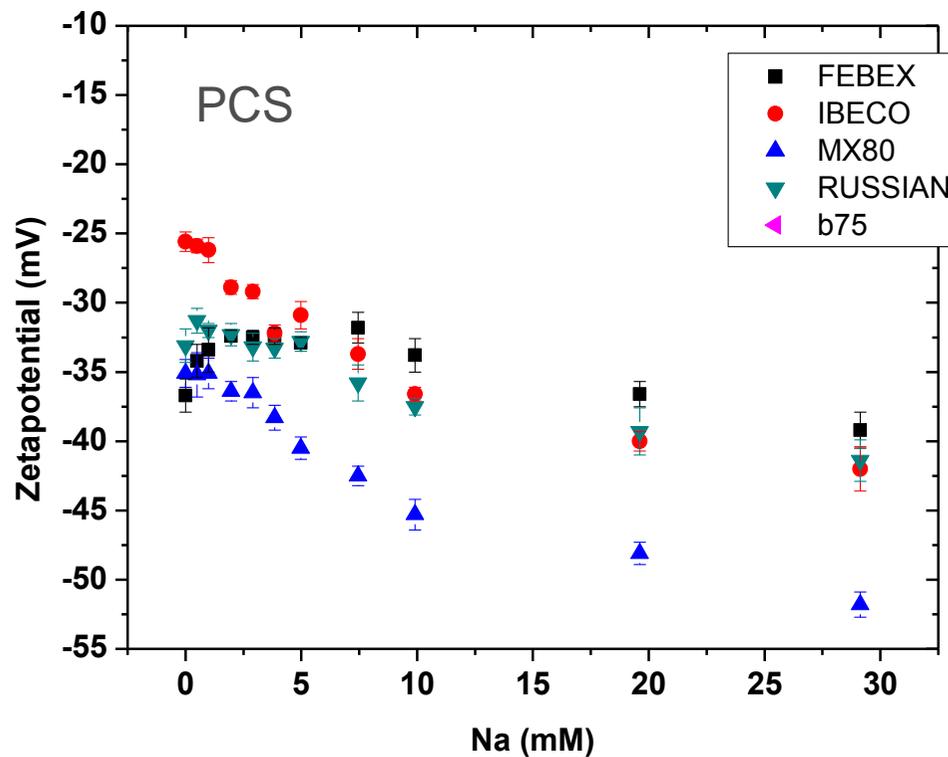


- For further stability studies and characterization five different bentonites were selected
 - FEBEX bentonite, Spain (Huertas et al., 2000)
 - IBECO bentonite, Mylos, Greece (Koch, 2008)
 - MX-80 bentonite, Wyoming, USA (Müller-Vonmoss and Kahr, 1983)
 - Bentonit 75 (denoted as B75), Rokle, Czech Republic (Konta, 1986)
 - Russian bentonite, Khakassia (Sabodina et al., 2006).
- A complete geochemical and mineralogical characterization was carried out (Fernandez, 2013)
 - mineralogy, especially clays content, cation exchange capacity and occupancy of cations on exchange positions, water content, porewater chemistry, charge distribution and cell formula
- Reason for detailed characterization of bentonites
 - One of the possible causes of the difference in the stability / erosion behaviour could be related to the different mineralogy (mainly clay minerals and its properties) of the different bentonites (tri-octahedral vs. di-octahedral clays, different exchange complex, different charge density, different charge location)
 - Try to find a trend or correlation between the bentonites characteristics and its stability

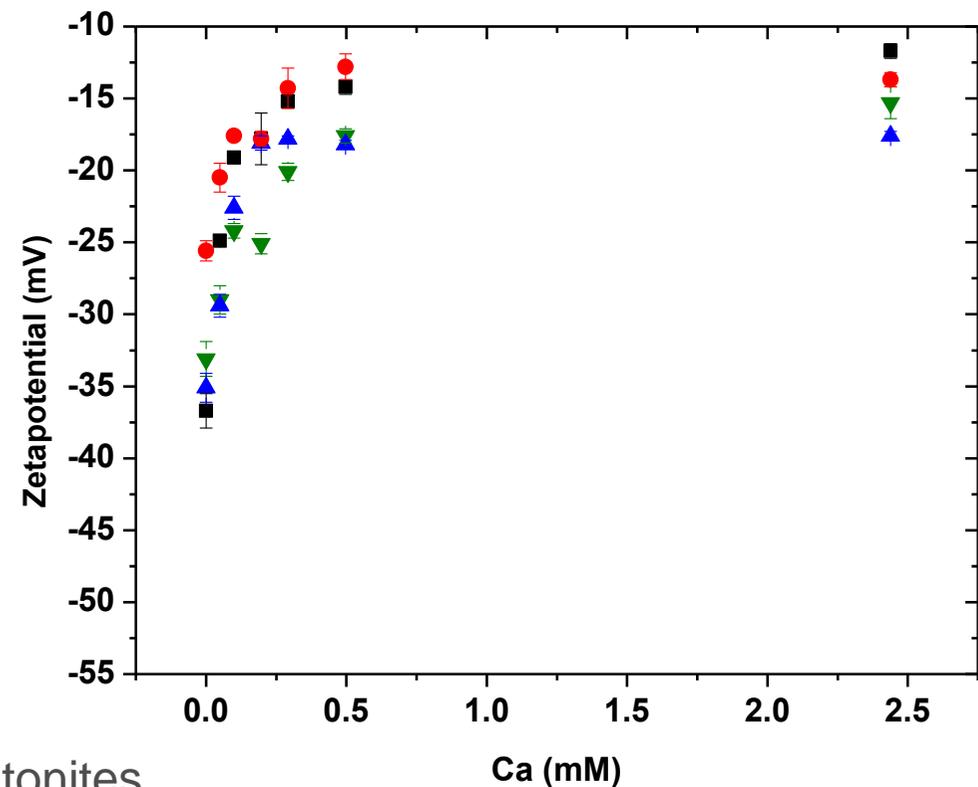
WP4: Role of inorganic compounds



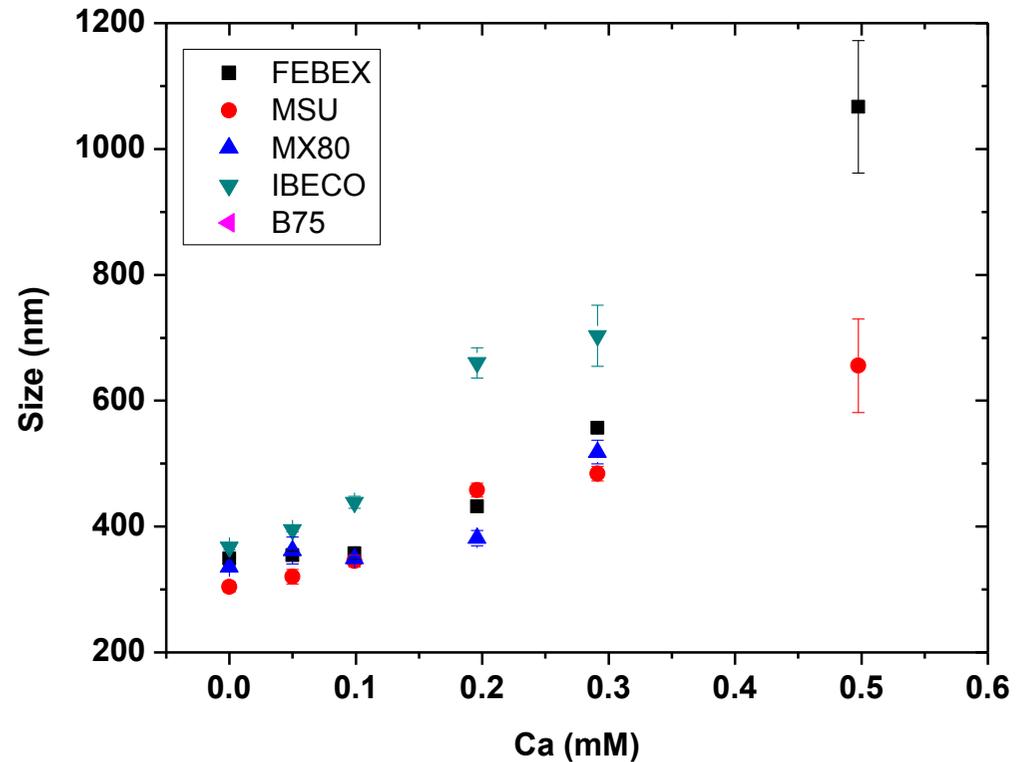
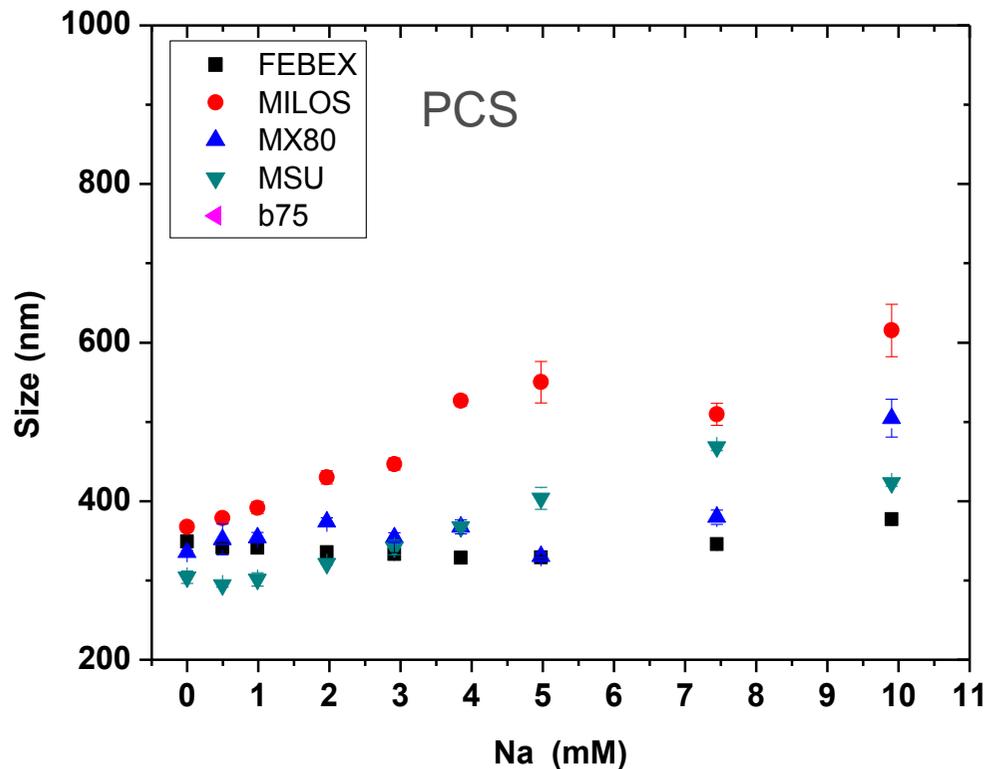
- Stability studies (effect of cations, anions, pH, admixtures – illite, kaolinite, Al_2O_3) measuring CCC (test-tube coagulation tests), particle size by PCS or PCCS and zeta-potential
- It has to be noted, that CCC tests must be evaluated taking exchange into account (uncertainties for raw bentonites)



raw bentonites



WP4: Role of inorganic compounds

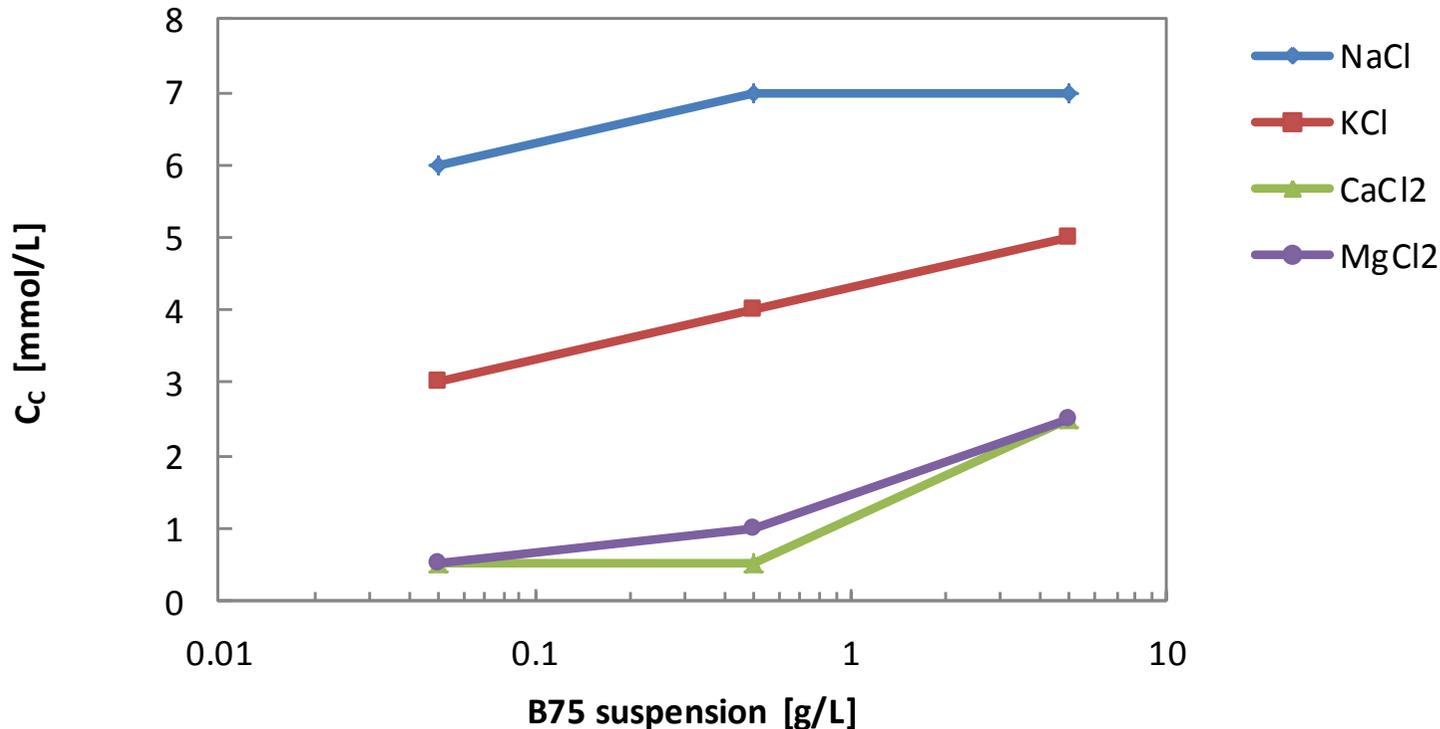


Clay colloid aggregation is triggered by the presence of Na (10 mM) or Ca (0.1-0.2 mM) in solution indicating that they will not be stable with higher concentration of these ions.

WP4: Role of inorganic compounds



CCC (test-tube coagulation tests)



Importance of divalent cations. The effect of increasing CCC with the solid content (concentration of bentonite in suspension).

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, see D4.7 (Hedström et al., 2014) and D4.8 (Alonso et al., 2015).

Hedström M., Gondolli J., Červinka R. (2014): Status report on the effects of various anions. Deliverable D4.7. BELBaR.

Alonso U., Missana T., Mayordomo N., Fernandez A.M., Gondolli J., Červinka R. (2015): Status report on the effect of different bentonite types (Rokle, Mx-80, Febex, etc) on clay colloid stability. Deliverable D4.8. BELBaR.

WP4: Role of inorganic compounds

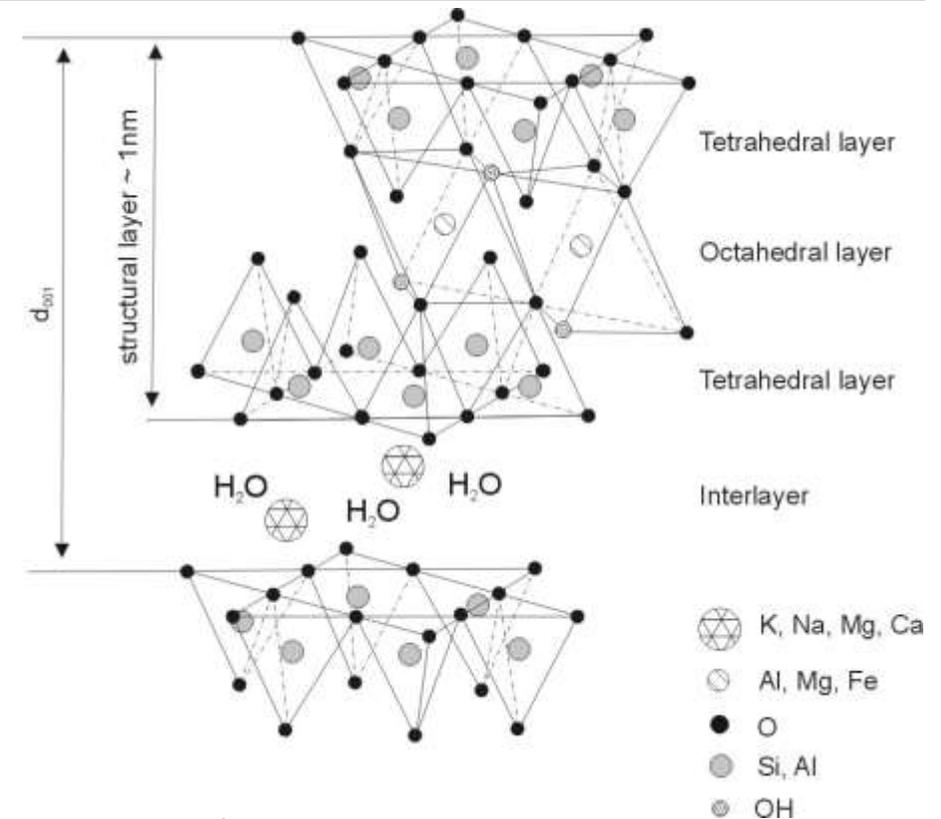


Estimated CCC varies among Na-montmorillonites from different origins. Hansen and Hedström (2014) performed stability experiments at a larger number of different NaCl concentrations, give the following CCC values: Wyoming Na-montmorillonite, Wy-Na (from MX-80), **20 mM** (up to 6% w/w); Milos Na-montmorillonite, Mi-Na (from Deponit CA-N), **6-8 mM** (up to 4% w/w) and for Kutch Na-montmorillonite, Ku-Na (from Asha 505), **~4 mM** (up to 4% w/w).

In general, those clays having the charge located in the tetrahedral layer forms larger colloids: these particles sediment easier being less stable than others even in DW. For more details see paper in preparation (Missana et al., 2016).

Karnland et al. (2006) SKB TR-06-30.

	Wy-Na1	Wy-Na2	Mi-Na1	Mi-Na2	Ku-Na
CEC [eq/kg]	0.87	0.88	0.97	1.09	1.04
σ [C/m ²]	-0.11(1)	-0.11(1)	-0.12(3)	-0.14(0)	-0.13(5)
Tetr. Charge [e]	-0.11	-0.05	-0.15	-0.27	-0.38
Octa. Charge [e]	-0.54	-0.60	-0.57	-0.55	-0.42
Total Charge [e]	-0.65	-0.65	-0.72	-0.82	-0.79



Hansen E., Hedström M. (2014): Colloidal pastes, gels and sols: State diagrams of three naturally occurring montmorillonites (to be submitted).

Missana T., Alonso U., Fernandez A.M. (2016): Stability behavior of natural clays: the importance of physico-chemical characteristics of the clay. In preparation.

■ Series of test-tube tests

- The C_c 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 for 50 mg/l)
- Different electrolytes (NaCl , NaNO_3 , Na_2SO_4 , Na_3PO_4 and MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, MgSO_4)

Salt	C_c (mmol/l)	$C_{c(\text{cation})}$ (mekv/l)	pH	First lower concentration below C_c (mmol/l)	PCCS ϕ_h (nm)
NaCl	5	5	6.3	not measured	not measured
NaNO₃	6	6	6.0	5	870
Na₂SO₄	3	6	6.1	2	approx. 1000
Na₃PO₄	no coagulation at given phosphate concentrations				

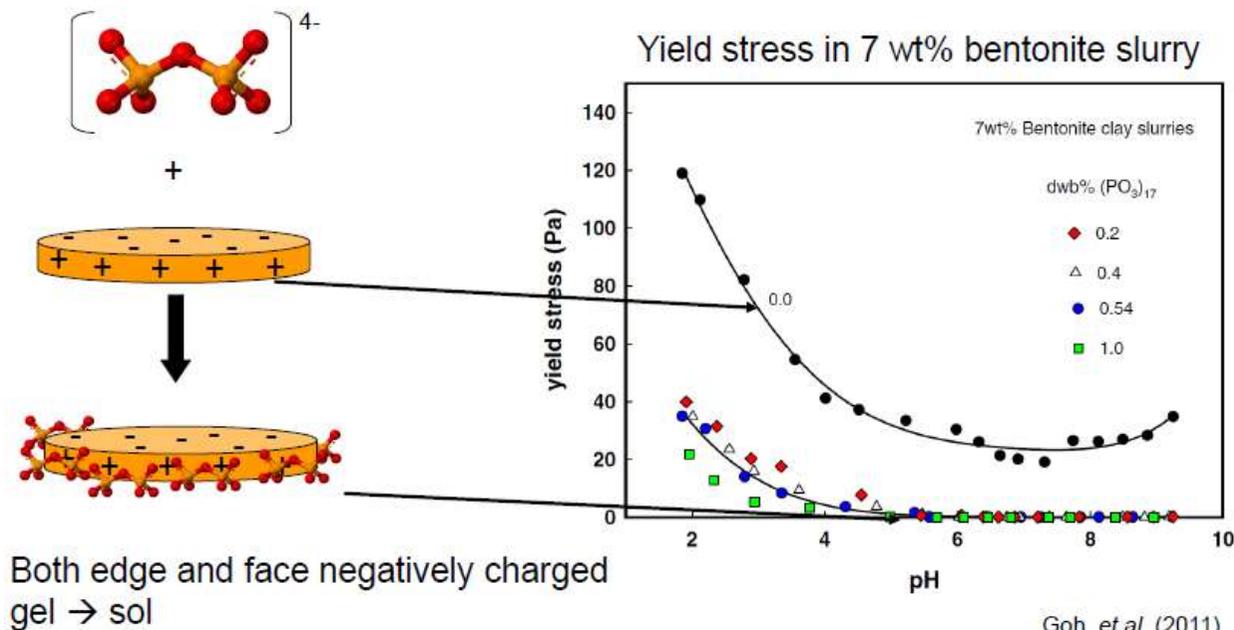
Salt	C_c (mmol/l)	pH	First lower concentration below C_c (mmol/l)	PCCS ϕ_h (nm)
MgCl₂	0.5	6.7	0.1	790
Mg(NO₃)₂	0.5	6.4	0.1	500
MgSO₄	0.5	6.1	0.1	476

ϕ_h - mean hydrodynamic diameter

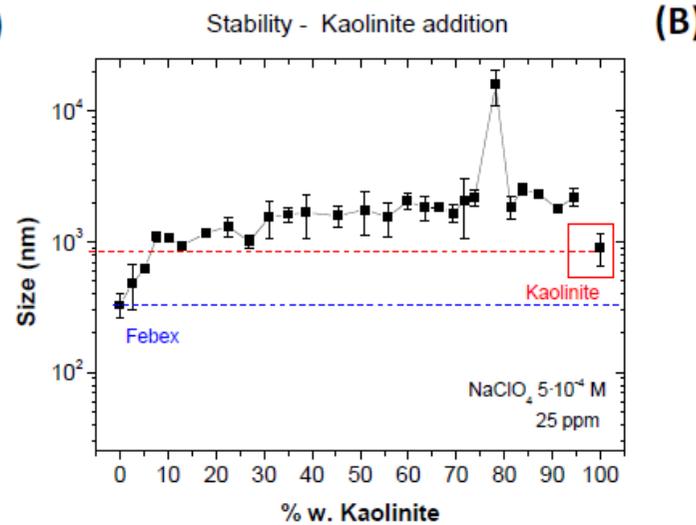
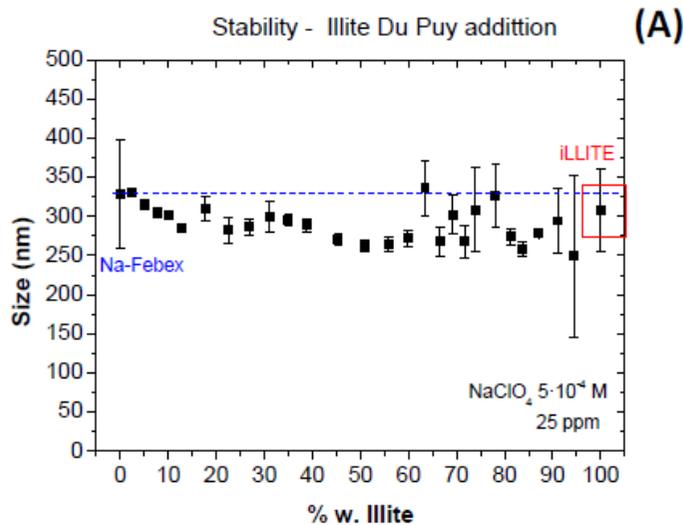
WP4: Role of inorganic compounds



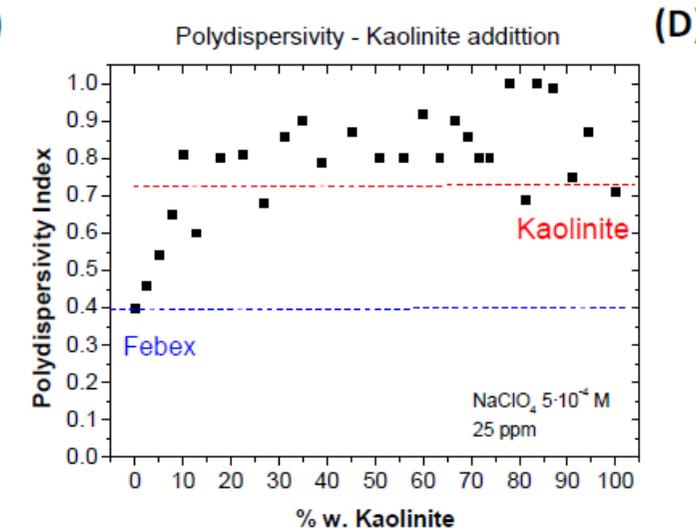
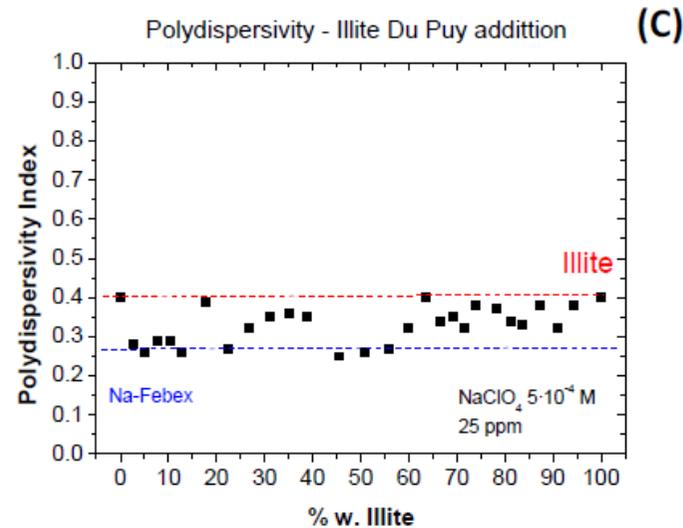
- Changing anion has only minor effect on the CCC, provided that the anion does not directly influence the overall clay particle charge, as in the case of polyphosphates and to some extent OH-, see D4.7 (Hedström et al., 2014).
- Exploring the influence of interacting anions may be of less direct practical significance for the safety assessment of a repository for spent nuclear fuel, but are of utmost importance for the understanding of the chemical-physical forces that hold gels together. The effect of polyphosphates on the gelling provide evidence that the gels are formed from edge(+)-face(-) attraction.



WP4: Role of inorganic compounds



(B) The interaction of smectite with mineral like kaolinite or Al_2O_3 produces the aggregation of particles that, alone under the same chemical conditions would be stable; this means that the presence of certain minerals not only inhibits the clay colloid generation “by dilution” of the smectite, but also may affect the properties of the smectite itself making the system unstable, D4.8 (Alonso et al., 2015).



WP4: (Ir)reversibility of coagulation process and hysteresis



- The disaggregation process of illite and smectite clays has been shown to be not completely reversible because the aggregation process is usually very rapid (minutes) but the kinetic of disaggregation, until reaching a complete disaggregated state, largely depends on the initial conditions of the experiments. The disaggregation process is more rapid in more diluted suspensions, D4.4 (Missana et al., 2014).
- During the investigations the effect of hysteresis was observed with different methods. The rheometry measurements showed that the attractive forces in the gels increase with aging. One week of resting produce significantly stronger gels than those tested after 24 hours, D4.9 (Hedström et al., 2015).

Average yield stress from the rheological measurements on Ku-mmt gels (from Asha 505)

C_{mnt} [NaCl]	Average maximum yield stress (Pa)			
	10 g/l, 24 h	10 g/l, 1 week	20 g/l, 24 h	20 g/l, 1 week
5 mM	0.4	1.1	4.4	7.7
10 mM	1.5	2.8	5.3	8.0
20 mM	-	-	9.2	8.9
50 mM	2.5	3.5	8.5	-
100 mM	2.6	3.9	10.0	-

Missana T., Alonso, U., Mayordomo, N., Benedicto A. (2014): Report on the reversibility of the coagulation process. Deliverable D4.4. BELBaR.

Hedström M., Nilsson U., Eriksson R. (2015): Rheology of attractive and repulsive montmorillonite/bentonite gels. Deliverable D4.9. BELBaR.

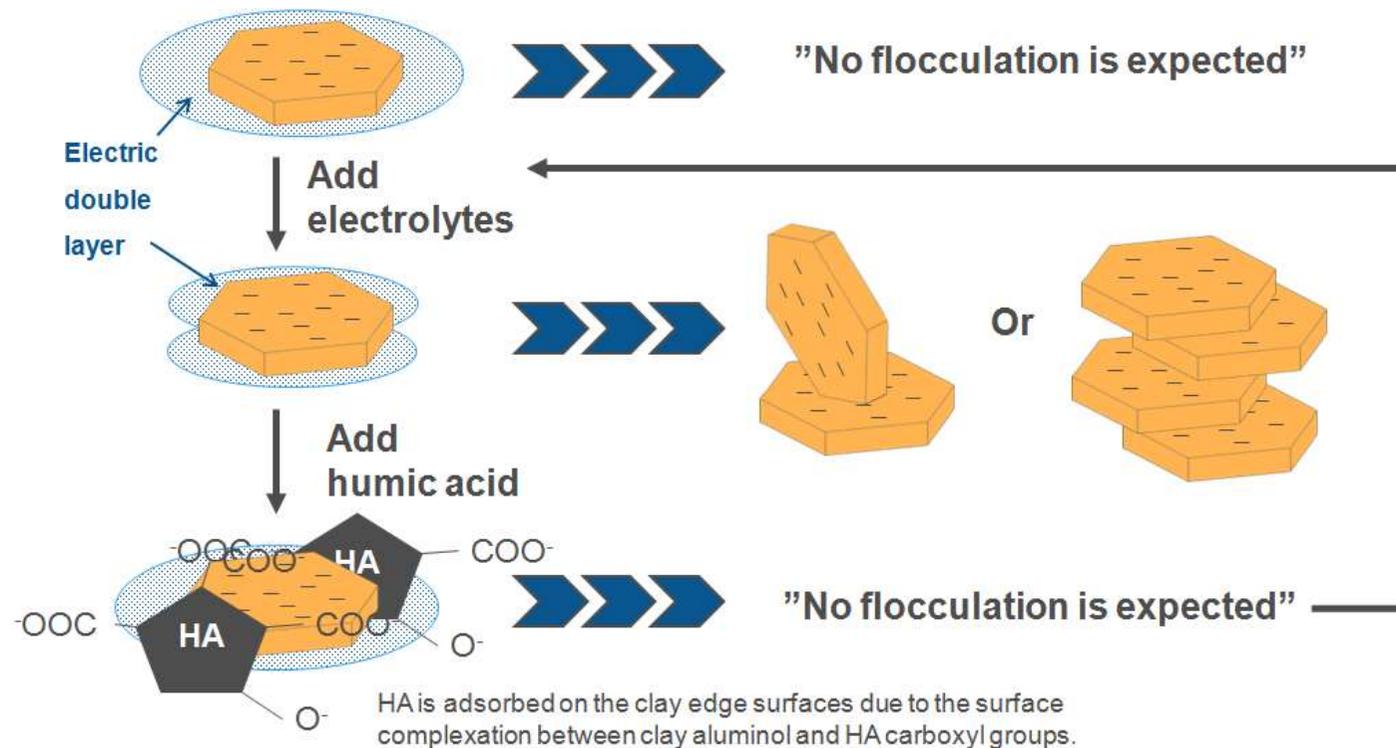
BELBaR Final Workshop

Berlin, 3-4 February, 2016

WP4: Role of organic compounds



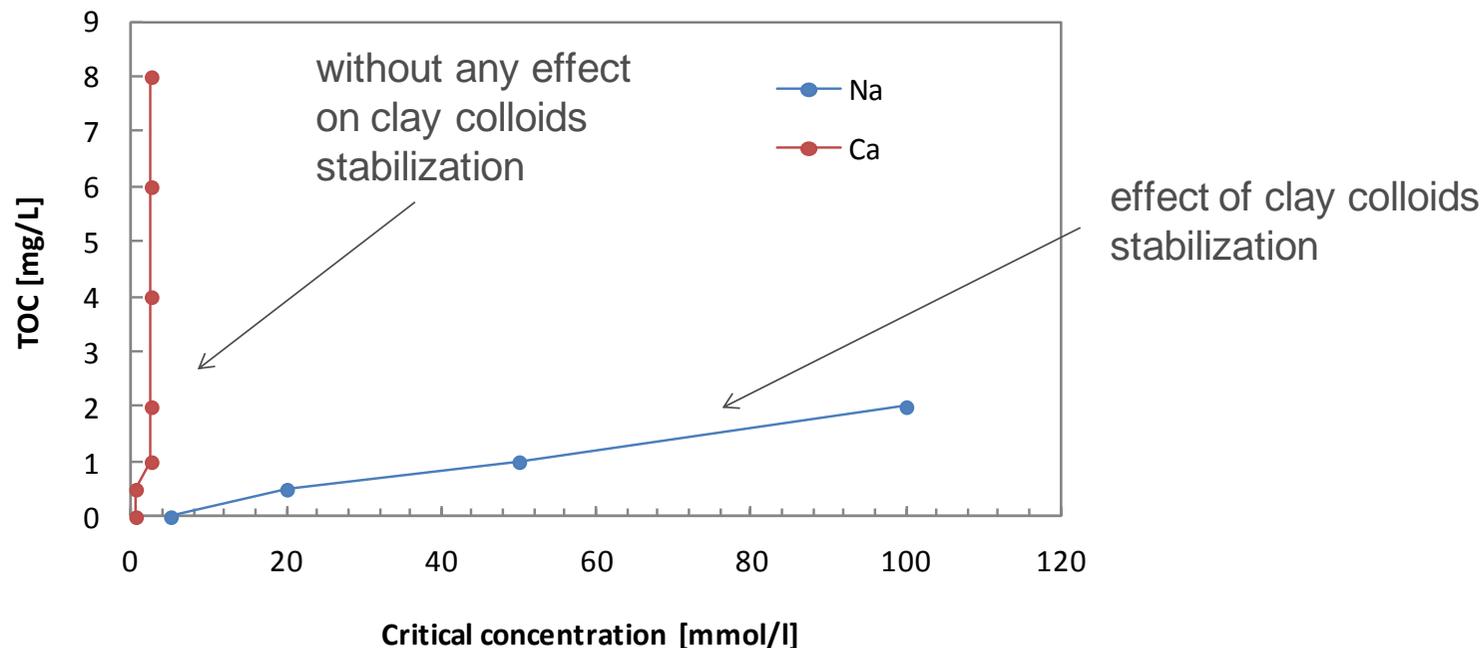
- The presence of organic substances in DGR is expected to be associated with host rock itself, microbial and anthropogenic activities and materials used in the construction.
- The interaction between the clay colloids and organic molecules greatly influences its stability.
- Studies were focused on humic and fulvic acids, which are natural organic substances often occurring in surface waters and near-surface groundwaters.



WP4: Role of organic compounds



- Organic matter (like humic or fulvic acids) is able to stabilize clay colloids in NaCl electrolyte (experimental concentration up to 0.1 M NaCl). This means that in presence of organic matter more concentrated NaCl electrolyte is needed to coagulate clay dispersion (the CCC is higher). For example the CCC is four times higher in a suspension containing 0.5 mg/L TOC compared to the same suspension without humic acid, see D4.6 (Bouby et al., 2014).



WP4: Role of organic compounds



- In all the other electrolytes investigated (CaCl_2 , MgCl_2) and at higher IS, the clay colloids undergo fast coagulation, independently of the presence of organic matter. This is true in various aqueous media containing different inorganic cations, showing that the IS remains the key parameter.
- Long term study tends to demonstrate that even under geochemical conditions where the colloids are expected to be stable, they may undergo a continuous slow agglomeration process.

WP4: The improvements of mechanistic model of bentonite swelling



- The theoretical basis for understanding of the effect of the Ca (divalent cation) on clay gel stability was summarised in D4.3 (Wang et al., 2013).
- A self-consistent weighted correlation approximation to density functional theory was developed (Wang et al., 2011a; Yang and Liu, 2015) to describe the structural and thermodynamic properties of counterion-only electrical double layers. The predictions agree well with the Monte Carlo simulations and show that the Ca-bentonite would behave essentially as the Na-bentonite when the fraction of surface charge neutralized by Na^+ is more than 30 %. It is known from experiments, that this boundary lies between 20-30 %.

Wang Z., Liu L., Moreno L., Neretnieks I. (2013): Status report on the theoretical understanding of the effect of the Ca on clay gel stability. Deliverable D4.3. BELBaR.

Wang, Z., Liu, L. and Neretnieks, I. (2011a): The weighted correlation approach for density functional theory: a study on the structure of the electric double layer, J. Phys.: Condens. Matter, 23, 175002.

Yang, G. and Liu, L. (2015): A systematic comparison of different approaches of density functional theory for the study of electrical double layers, J. Chem. Phys., 142, 194110.



Oral presentation (Feb. 4): Interaction pressure between charged plate-like particles in electrolyte solutions: An application of density functional theory with the solvent primitive model - Longcheng Liu

BELBaR Final Workshop
Berlin, 3-4 February, 2016

WP4: List of deliverables (PU)



N°	Title	Responsible organisation	Nature	Dissemin. level	Delivery date
D4.1	State-of-the-art report on experimental techniques used for investigations of clay colloid stability, including an establishment of protocol for rheology and turbidity experiments	ClayTech, CIEMAT, KIT-INE, NRI-Rez	R	RE	09/2012 (6 M)
D4.2	Progress Report on the effect of pH on clay colloid stability	CIEMAT, KIT-INE, NRI-Rez, ClayTech	R	PU	05/2013 (15 M)
D4.3*	Status report on the theoretical understanding of the effect of Ca on clay gel stability	KTH	R	RE	05/2013 (15 M)
D4.4	Status report on the reversibility of the coagulation process	CIEMAT	R	PU	06/2014 (27 M)
D4.5	Status Report on colloid stability and DOC effect	KIT-INE	R	PU	06/2014 (27 M)
D4.6	Status Report on influence of complexing agents on clay colloid stability	NRI-Rez, KIT-INE	R	PU	06/2014 (27 M)
D4.7	Status report on the effect of various anions	ClayTech, CIEMAT, KIT-INE, NRI-Rez	R	PU	06/2014 (27 M)
D4.8*	Status report on the effect of different bentonite types (Rokle, Mx-80, Febex, etc) on clay colloid stability	CIEMAT, KIT-INE, NRI-Rez, ClayTech	R	PU	06/2015 (39 M)
D4.9*	Rheology of attractive and repulsive montmorillonite/bentonite gels.	ClayTech	R	PU	06/2015 (39 M)
D4.10*	Effects of different mechanisms/factors on colloid stability of dispersions of calcium dominated bentonites in dilute solutions	KTH	R	PU	06/2015 (39 M)
D4.11	WP4 partners final report on experimental results on clay colloid stability	NRI-Rez, All	R	PU	11/2015 (44 M)

Publication plan



- **Deliverable 6.6 Development of a publication plan for the publication of peer reviewed project results in high-quality journals**
 - There is 46 planned or already published papers....

Acknowledgement



- To organizations for fruitful results and cooperation in WP4



- To SKB for project coordination



- 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.