BELBaR Project

WP4: Clay colloid stability Introduction

Radek Červinka
ÚJV Řež, a. s., 2015

CP BELBAR WP4 MEETING
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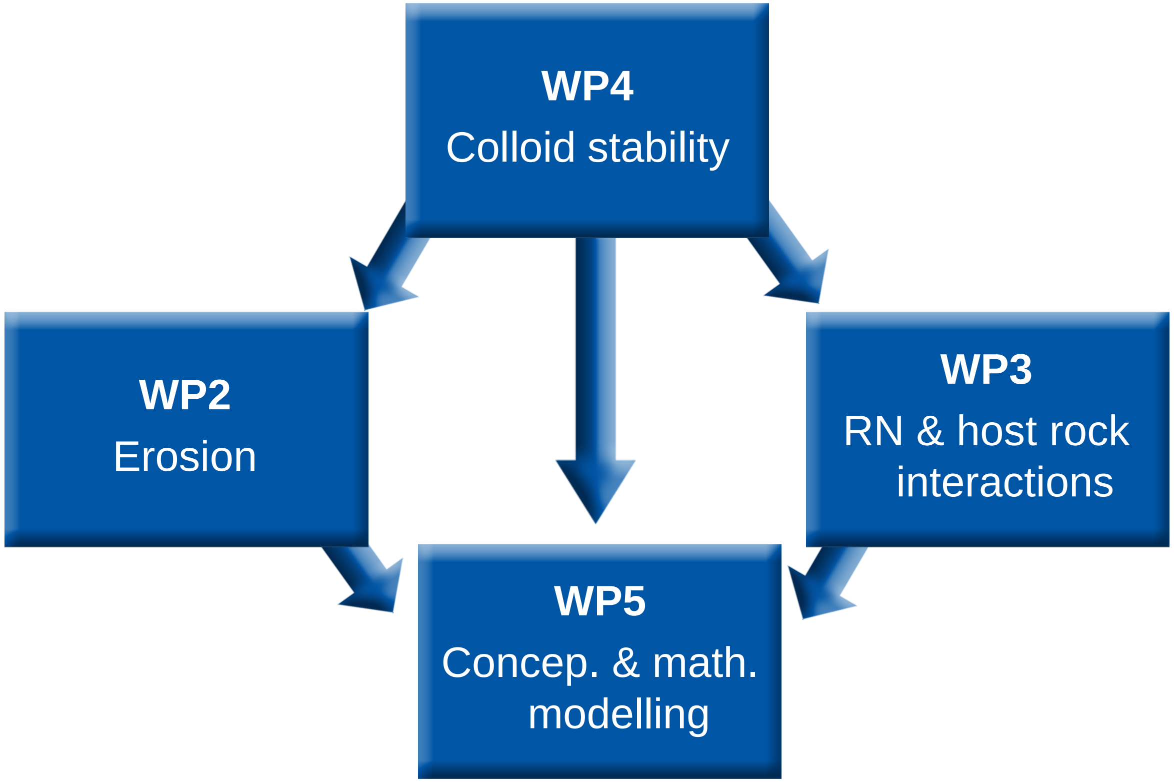
WP4: Objectives



Clay colloid stability studies under different geochemical conditions with respect to ionic strange and pH

Critical coagulation concentration, coagulation kinetics, (ir)reversibility of coagulation process

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

WP4: Partners participation, goals

- **Experimental programme on clay colloid stability**
  - **KIT-INE** performed **long time period studies** on colloids stability with **MX-80** in presence of different electrolytes, pH, tetravalent actinide element Th(IV), Fe, fulvic acid. Large set of samples. Start in 2013 till the end of project. See progress report D4.5
  - **CIEMAT** compared the stability of clay colloid suspensions of different bentonites (**FEBEX, Mylos, MX-80, B75, Russian bentonite**) as a function of pH (D4.2). Also the comparative study on bentonites characteristics was performed (D4.8). CIEMAT also focused on (ir)reversibility of coagulation process (D4.4)
  - **ÚJV** studied the **coagulation of dilute clay dispersions** by cations, anions (see D4.7) and influence of humic substances on coagulation process (D4.6). Bentonite **B75, BaM** (CZ)
- **Rheology experiments (sol-gel transition)**
  - **ClayTech** defined recommendations for rheology measurement in D4.1 and the rheological measurements were summarized in (D4.9), bentonite/montmorillonite **Asha505,** with contribution of **B+Tech.**
  - **B+Tech** input of relevant information from WP2
- **Theoretical basis**
  - **KTH** summarized in general the theoretical background for methods of statistic mechanics that have considered the ion-ion correlation effect to quantify the swelling between inter-lamellar layers and to investigate the role of divalent ions such as Ca on the structure of smectite particles (D4.3, D4.10 is pending)

WP4: Partners and PM's

Work package number	4	Start date or starting event:				Project Month 1
Colloid stability						
Activity Type	RTD					
Participant	CIEMAT	KIT-INE	NRI-REZ	SKB	ClayTech	KTH	B-Tech
Person-months for the participant	6	7	7	1	9	28	1

- 7 partners total
- 5 partners with research program, 2 partners as „observers"
- SKB: cooperate with or support KTH and Clay Technology
- B-Tech: following the work and contribute relevant observations from their experimental work in WP2

WP4: Deliverables

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)	Submitted
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)	Submitted
D4.3*	Status report on the theoretical understanding of the effect of Ca on clay gel stability	**KTH**	R	RE	05/2013 (15 M)	Submitted
D4.4	Status report on the reversibility of the coagulation process	**CIEMAT**	R	PU	06/2014 (27 M)	Submitted
D4.5	Status Report on colloid stability and DOC effect	**KIT-INE**	R	PU	06/2014 (27 M)	Submitted
D4.6	Status Report on influence of complexing agents on clay colloid stability	**NRI-Rez**, KIT-INE	R	PU	06/2014 (27 M)	Submitted
D4.7	Status report on the effect of various anions	**ClayTech**, CIEMAT, KIT-INE, NRI-Rez	R	PU	06/2014 (27 M)	Submitted
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)	Submitted
D4.9*	Rheology of attractive and repulsive montmorillonite/bentonite gels.	**ClayTech**	R	PU	06/2015 (39 M)	Submitted
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)	In progress?
D4.11	WP4 partners final report on experimental results on clay colloid stability	**NRI-Rez**, All	R	PU	11/2015 (44 M)	

WP4: Agenda

Time slot	Partner (PM's)	Theme suggestions
5 min	ÚJV	Introduction and expectations based on WP 1
20 min	CIEMAT (6 PM's)	- influence of different bentonite properties on clay colloid stability - (ir)reversibility of coagulation process and its kinetics
20 min	ÚJV (7 PM's)	- the stability of clay colloids in groundwater (CCC)
20 min	KIT-INE (7 PM's)	- role of humic substances on clay colloid stability - long-term studies on clay colloid stability
20 min	ClayTech (9 PM's)	- sol-gel transition for varying Na/Ca ratio in montmorillonites
20 min	KTH (28 PM's)	- explanations for different behaviour of Ca-bentonites
20 min	ÚJV	Wrap up for WP1

- The „theme suggestions“ come out from the planned activities of individual partners in WP4. The list of presentations is little bit reorganized. The main conclusions should be transformed to answers according to WP1 issues (next two slides).

Synthesis of issues: Colloid stability (WP4)

Issue	Safety case position at start of BELBaR	Outcomes sort for final State-of-art report
Colloid stability controlling processes	Stability of compacted bentonite in dilute porewater conditions has been evaluated by laboratory measurements. The controlling process is hydration of exchangable cations limited by the availability of cation free water. Currently the uncertainties in geochemical conditions are greater than in uncertainties in the stability limit. Colloid stability studies have found that model colloids that possess a significant net negative charge at neutral pH, i.e. silica and illite clay, show the greatest stability under neutral pH conditions.	Understanding of the processes controlling colloid stability and their representation in the safety case (WP4).

WP4: Synthesis of issues

Synthesis of issues: Colloid stability (WP4)

Issue	Safety case position at start of BELBaR	Outcomes sort from WP
Influence of other factors to colloid stability	Accessory minerals seem to enrich near the bentonite-groundwater interface. Filtration has been discussed as a possible mean to reduce erosion. Colloid size, solution ionic strength and water flow rate are factors which strongly influence colloid migration. Association of inorganic particles with natural organic compounds is an important mechanism for colloid stabilisation. This mechanism could potentially operate to stabilise and enhance colloid populations in the near-field porewater, this remains an area of uncertainty.	Summary of the influences of these factors on colloid stability, to what extent are they significant for the safety case?

Wrap up for WP1:

- **Critical coagulation concentration, coagulation kinetics, (ir)reversibility of coagulation process**
  - The CCC of NaCl varies among Na-montmorillonites from different origins -> differences in layer charge (CEC) and its distributions???
  - Effect of anions ??? SO_4^{2-}
  - Coagulation tests must be evaluated with taking cation exchange into account.
  - Both the “melting” experiments and rheometry show that the attractive forces in the gels increase with aging. The phase diagrams.
  - Minor influence of pH on gel stability, strength of attractive gel increases with clay content,
  - 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. Hysteresis.

Wrap up for WP1:

- **Clay colloid stability studies under different geochemical conditions with respect to ionic strange and pH**
  - Complete geochemical and mineralogical characterization of used bentonites
  - The main properties (size and zetapotential) of colloids extracted by all the analyzed bentonites are similar. They show very similar zeta-potentials (around -35 mV); their size ranges from 200 to 500 nm and it remains unvaried up to $I=1\cdot10^{-3}$ M (in $NaClO_4$); colloids start aggregating at 0.01 M and at I=0.1 M they are completely destabilized with size outside the colloidal range (>1μm). Nevertheless they showed different capability of forming colloids in erosion tests (WP2).
  - It has been observed that the presence (in certain proportion) of minerals like kaolinite or oxides (alumina) causes the rapid aggregation of bentonite colloids.
  - Large scale experiment in GTS, Febex gallery – low generaiton of colloids due to geochemical conditions
- **Role of organic compounds (humic substances) on clay colloid stability**
  - The presence of HA significantly increases the colloidal stability of bentonite particles in case of NaCl electrolyte. In case of $CaCl_2$ electrolyte only minor effect occurred. It seems that the stabilizing effect of humic acid is different for univalent and divalent cations.
  - Long-term experiments of KIT-INE (ongoing)

Wrap up for WP1:

- **Theoretical basis and model evolution**
  - Preparation and validation of model
  - A self-consistent weighted correlation approximation to density functional theory was developed to describe the structural and thermodynamic properties of counterion-only electrical double layers. The predictions agree well with the Monte Caro 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%.