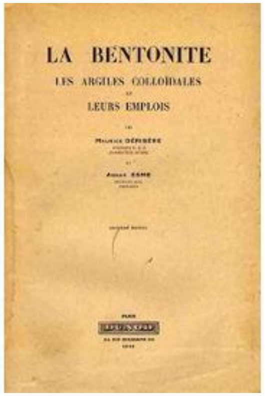
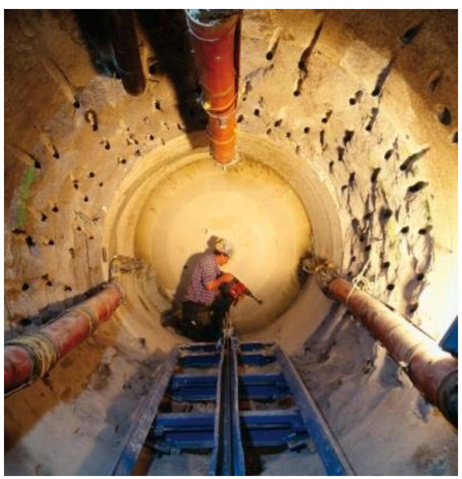

LA BENTONITE
LES ARGILES COLLOIDALES
LEURS EMPLOIS

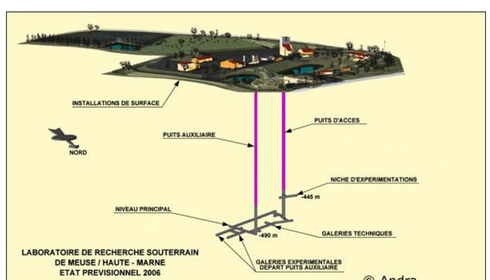
Contribution to the WP4

Muriel Bouby, Karin Norrfors, Yasmine Heyrich

4th BelBar Meeting

KIT-CN, 12-13 October 2015





WP4 KIT-INE work description

Systematic colloid stability studies: pH, low IS, OM

KIT-INE: Systematic colloid stability studies will be performed by **KIT-INE** to investigate the **pH, ionic strength and especially the organic matter effects** on bentonite clay colloids (MX-80) stability over **long time period (4 years)** under **glacial melt water conditions**.

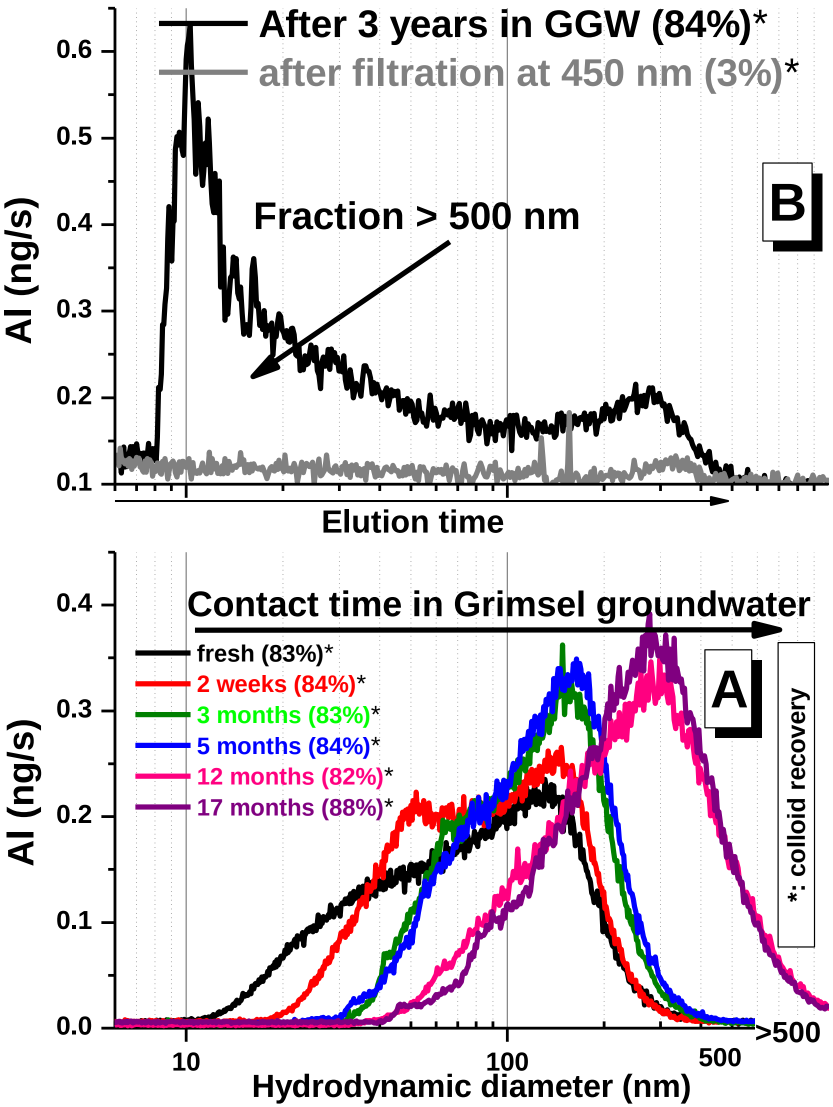
Measurements on the influence of DOC (Fulvic acids) on clay colloid stability (Ca- and Na-CCC) are needed to reduce the uncertainty in potential additional stabilizing effects naturally occurring. Experimental methods will include time resolved dynamic light-scattering (PCS) for fast coagulation studies (stability ratio W and critical coagulation concentration CCC) and AsFlFFF/ICP-MS for the slow coagulation rates expected under stabilizing conditions (glacial melt water) together with laser- induced breakdown detection (LIBD).

Why ?

Contradicting results showing that the low IS and high pH conditions of the Grimsel GW were not sufficient to fully stabilize clay colloids: Long-term agglomeration demonstrated

EXAMPLE 1

Al-fractograms evolution (size, recov.)

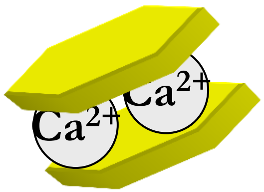


Bouby et al. GCA 75(13), 3866 (2011)

1- Slow agglomeration process over 3 years, reproducible

2- Explanations:

- Ca^{2+} ions induce agglomeration

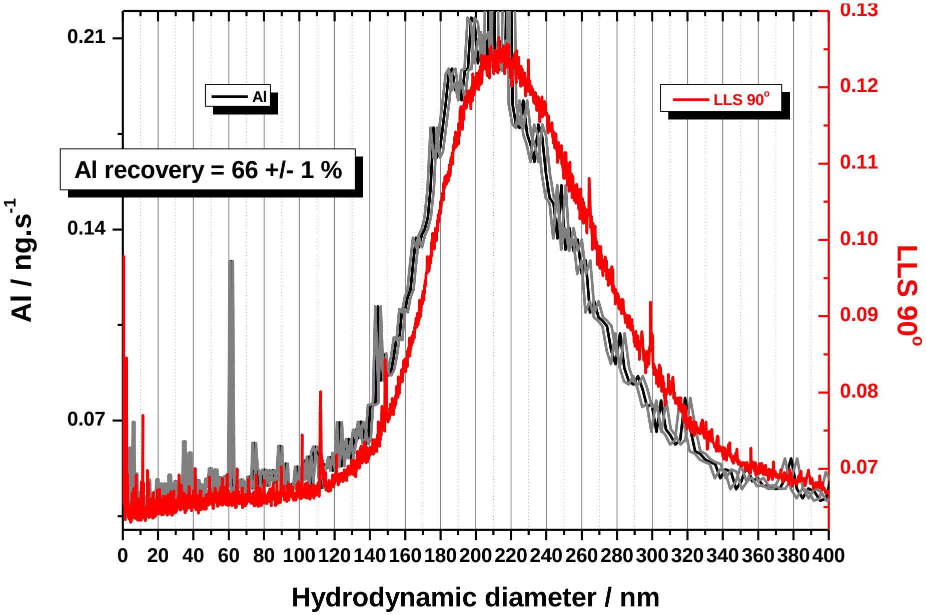


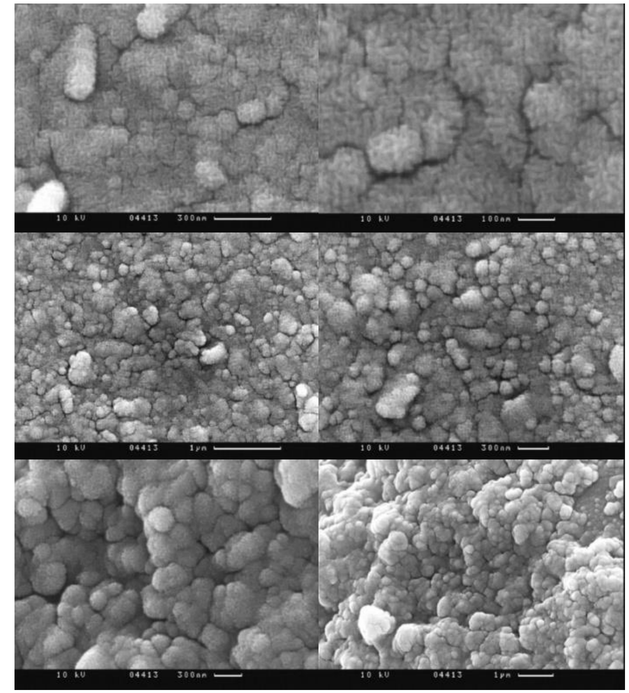
- CCC = 10^{-3} M in $CaCl_2$ (Seher et al. 2010)

At 3.3 10^{-4} M, pH 9-10, W~ 100; colloid - colloid collision efficiency = 1%

➜ *Slow clay colloid agglomeration not surprising*

EXAMPLE 2





Colloidal fraction + huge aggregates found in a 10 y old FEBEX bentonite colloid solution stored in a brown PET, pH_f 8.0

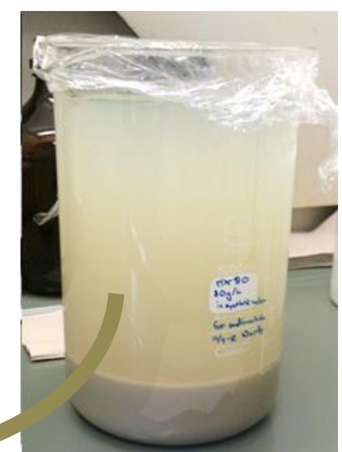
- **SEM pictures**

Clay colloid size heterogeneity effects on their stability (PhD work K.K. Norrfors)

➢ **Raw MX80 fractionated in a carbonated SGW**

- SKB Report TR-99-06
- SKB report TR-06-31
- SKB Report R-06-105
- SSM Report 2011:22

- pH = 8.4
- Ionic strength 1.26 10^{-3}M
- Na^{+} 1.2 mM – 28.4 mg/L
- Ca^{2+} 0.05 mM – 1.5 mg/L
- F^{-} 0.1 mM – 2.8 mg/L
- Cl^{-} 0.074 mM – 2.64 mg /L
- SO_4^{2-} 0.04 mM – 4.13 mg/L
- Si traces
- HCO_3^{-} 1mM – 84 mg/L



7 montmorillonite colloidal suspensions

Clay colloid size heterogeneity effects on their stability (PhD work K.K. Norrfors)

- **Raw MX80 fractionated in a carbonated SGW: 7 suspensions**
- **Detailed characterization**
- **Mean ESD : ~ 960 nm down to 85 nm**
- **Mean number edge sites estimation (factor up to 6)**
- **NaCl, $CaCl_2$, $MgCl_2$ stability tests, with or without OM: no evidence of a specific size effect observed**

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Research paper

Montmorillonite colloids: I. Characterization and stability of dispersions with different size fractions

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Clay colloid size heterogeneity effects on their stability (PhD work K.K. Norrfors)

- **NaCl, $CaCl_2$, $MgCl_2$ stability tests, with or without OM: no evidence of a specific size effect observed**

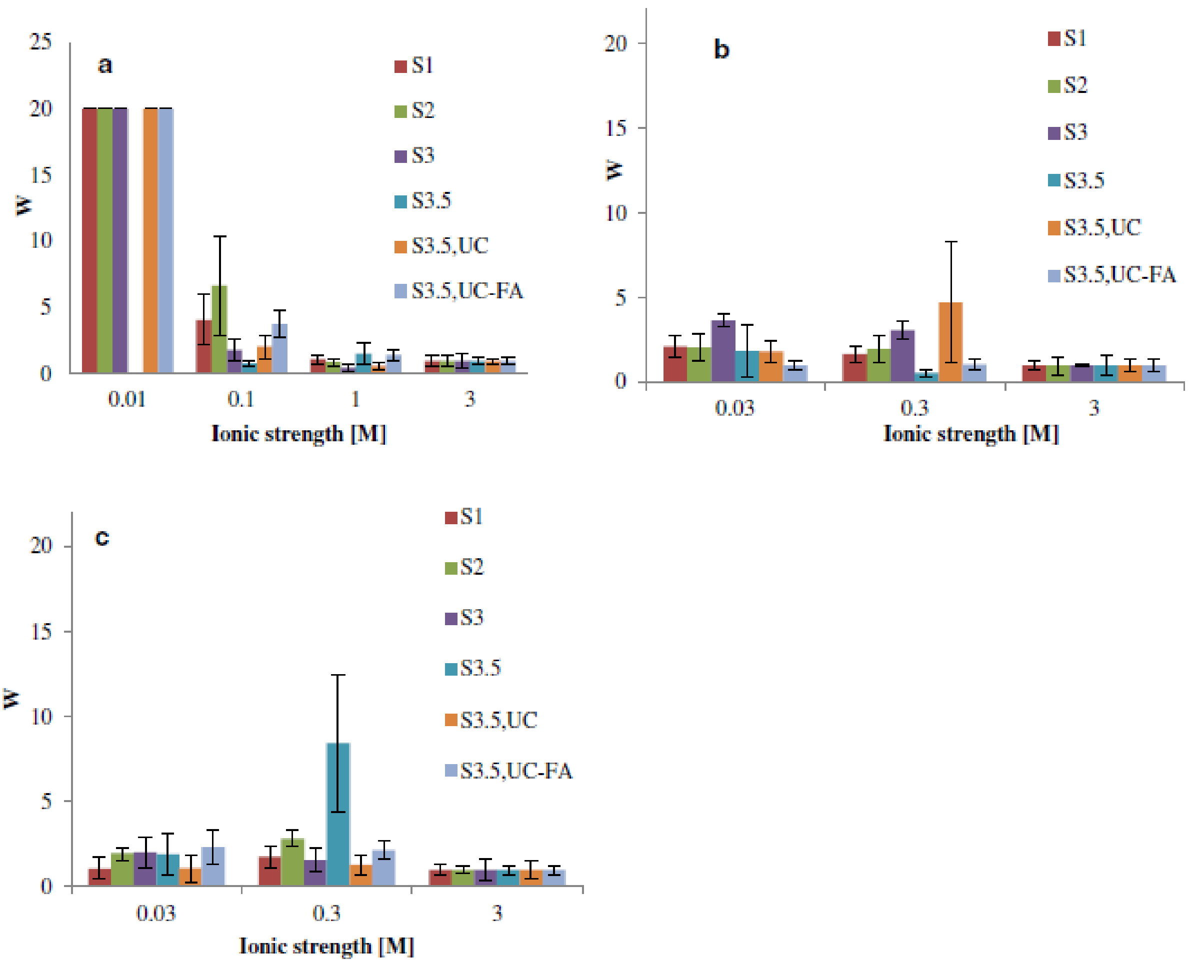


Fig. 6. Stability ratios for the colloidal dispersions after the addition of a) NaCl, b) $CaCl_2$ or c) $MgCl_2$, at pH 7. Infinity is set to 20 in the figures.

Systematic colloid stability studies: pH, low IS, OM

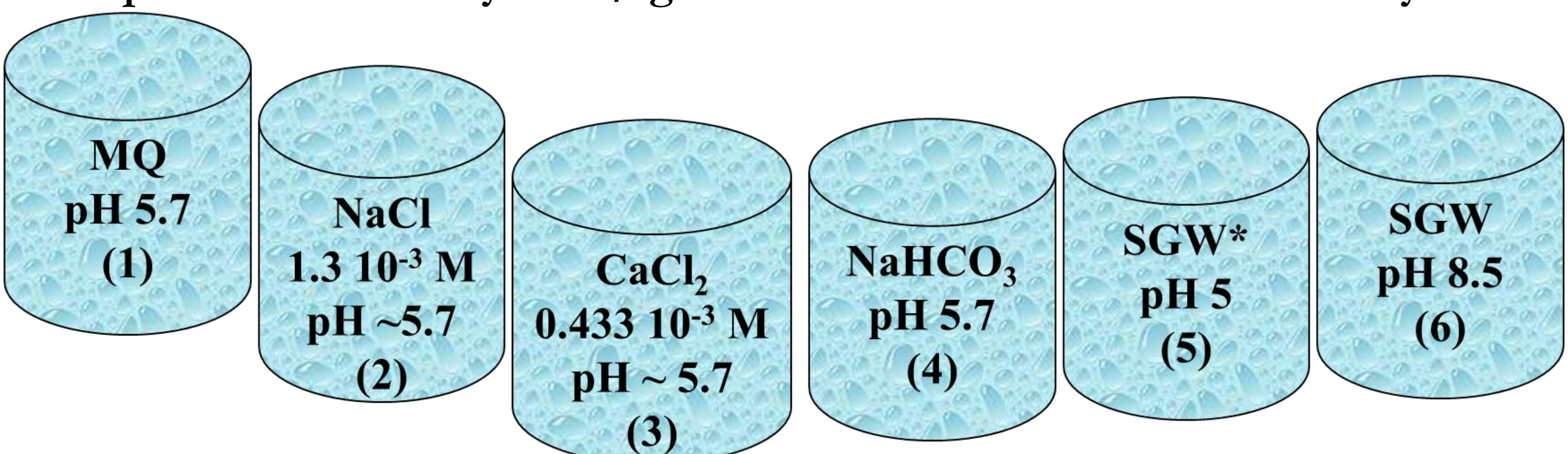
• *1 montmorillonite size fraction*

- ✓ Raw MX80 (Volclay)
- ✓ Sieving (Fraction < 63 µm used)
- ✓ (6 times) 10 g in 1 L LiCl 1 M (homo-ionisation, delamination)
- ✓ Contact time : 1 week under slow stirring

- ✓ Repartition in 50 mL tubes followed by a centrifugation at 35‘ at 3500 rpm
- ✓ Removal of the 1st supernatant

✓ 3 other extraction cycles consisting on:

a re-suspension of the clay solid/ gel-like residues in 6 different electrolytes



*: no HCO_3^- added

Systematic colloid stability studies: pH, low IS, OM

• *1 montmorillonite size fraction*

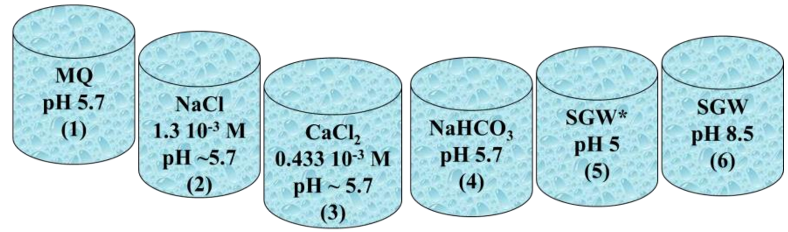
First characterization of the 6 clay colloidal stock suspensions (the 4th supernatants)

Electrolyte	[Colloids] 4th supernatant	pH 4th supernatant	Size range nm (PCS)
MQ	1.95 $g \cdot L^{-1}$	9.9	270-300
NaCl 1.3 10^{-3} M	1.38 $g \cdot L^{-1}$	9.9	240-300
$CaCl_2$ 0.433 10^{-3} M	1.56 $g \cdot L^{-1}$	9.9	
$NaHCO_3$ 10^{-3} M	1.59 $g \cdot L^{-1}$	9.6	270-310
SGW pH ~ 8.5	0.92 $\cdot L^{-1}$	9.3	290-350
SGW ~ pH 5	0.87 $g \cdot L^{-1}$	9.7	270-320

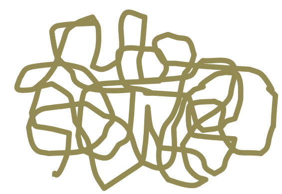
- [Si]/[Al] and [Al] /[Mg] ratios suggest the release of clay colloids
- Their size is in the range expected, further investigations are necessary to check the presence of smaller-sized particles
- The composition of the SGW strongly decreases the clay colloid production

Systematic colloid stability studies: pH, low IS, OM
• *1 montmorillonite size fraction*

- **Dilution of each of the 6 stock suspensions in the corresponding electrolytes …**



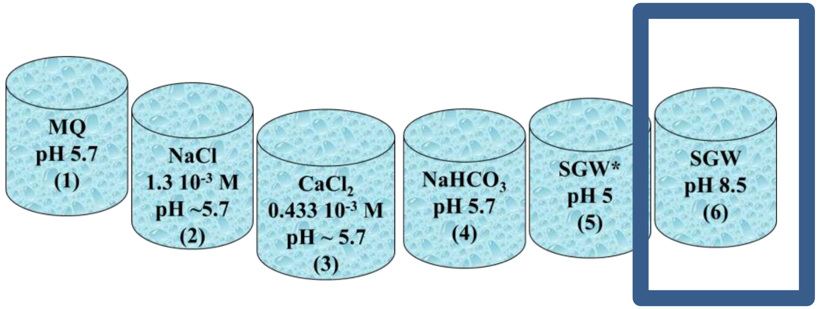
- **Containing or not additional FA [10 mg.L^{-1}]**
    - ✓ **[Colloids]: 1, 5, 10, 100 mg.L^{-1}**
    - ✓ **Colloids [10 mg.L^{-1}] + Fe^0 (~ 3 mg)**
    - ✓ **Colloids [10 mg.L^{-1}] + Th (10^{-8} M)**

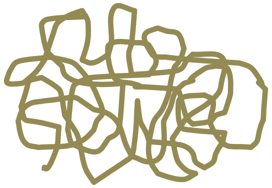
\+  **GOHY-FA-573**

- **12 samples are available for each set of conditions**
- **Storage at room temperature (~21-22°C)**
- **Samples are now 28 months old**

Training course tomorrow…A4F/UV-Vis./ICPMS

- Dilution of each of the 6 stock suspensions in the corresponding electrolytes …
- Containing or not additional **FA [10 mg.L^{-1}]**
  - ✓ [Colloids]: 1, 5, **10**, 100 mg.L^{-1}



\+ 

On-going:

- **Size and concentration evolution (fresh vs old samples)**
- **Th sorption reversibility test**

Future work:

- **Interaction with RNs (AsFlFFF/ICPMS, TRLFS, EXAFS, …)**
- **Iron effect**
- **Long time (28 months) delamination in LiCl 1 M**

WP4: Synthesis of issues

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).

pH, low IS, OM

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?


obrigado
Dank U
Merci
mahalo
Köszi
спасибо
Grazie
Thank you
mauruuru
Takk
Gracias
Dziękuję
Děkuju
danke
Kiitos