CIEMAT Outcome

WP4: STABILITY

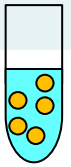
Ursula Alonso, Tiziana Missana, Natalia Mayordomo

Ana María Fernandez

Issue	Safety case position at start of BELBaR	Outcome
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).

Colloid stability
Colloidal particles < 1 um
Not aggregating

Batch



CIEMAT outcome

Issue	CIEMAT Outcome
Colloid stability controlling processes	✓ Compared behaviour of different bentonites:

FEBEX bentonite

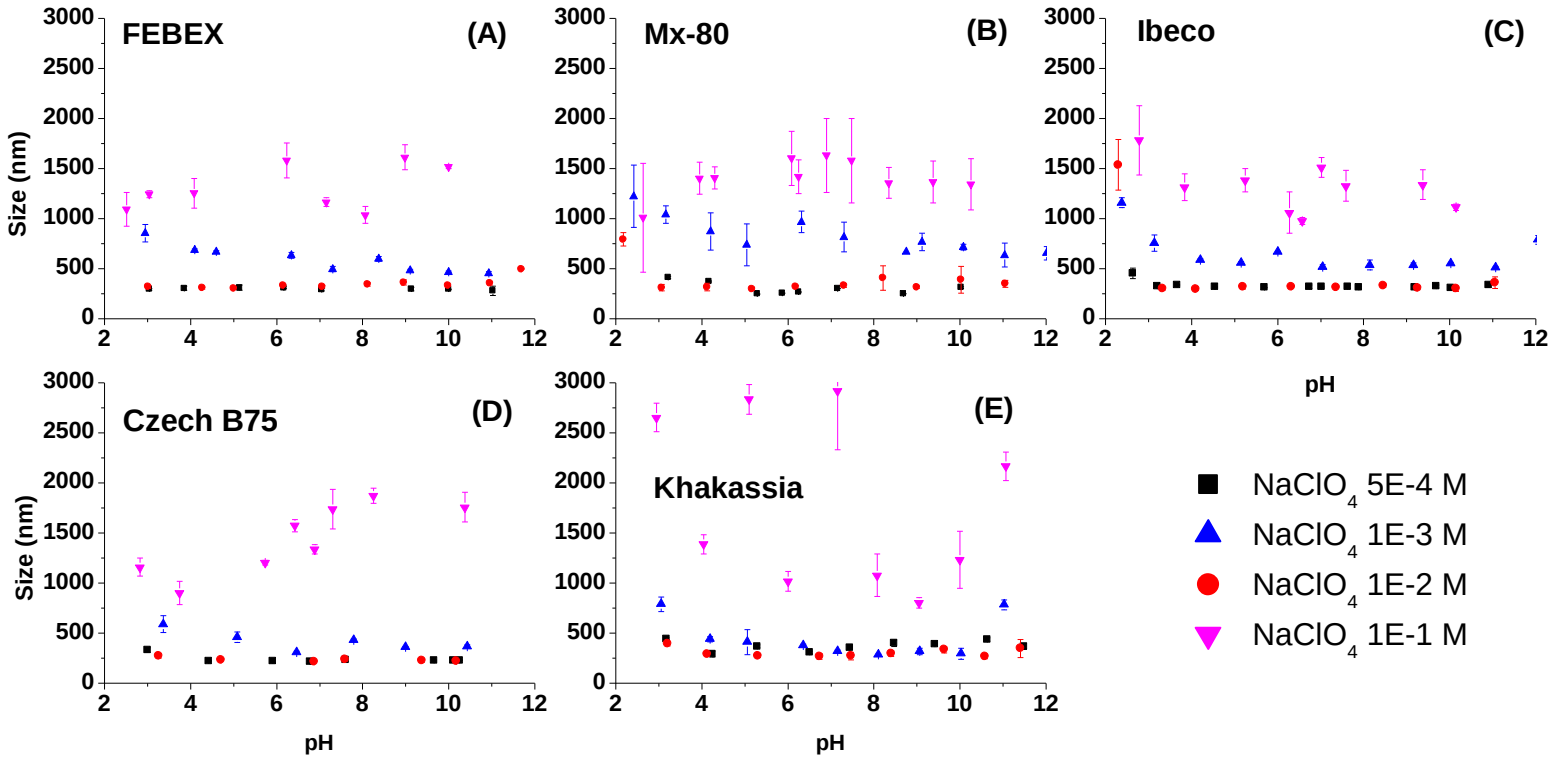
- Raw bentonites: MX80, Mylos - G, Rockle B75 -CzR, MSU- Russian, Nanocor
- Mixed clays: Kaolinite, Saponite, Zeolite, Illite, Oxides

✓ **Complete geochemical and mineralogical characterisation** was carried out, by different techniques:

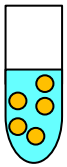
- **Mineralogy**
- **Clays content,**
- **Cation exchange capacity,**
- **Exchangeable cations,**
- **Pore water chemistry,**
- **Charge distribution**
- **Cell formula.**

⇔ EROSION

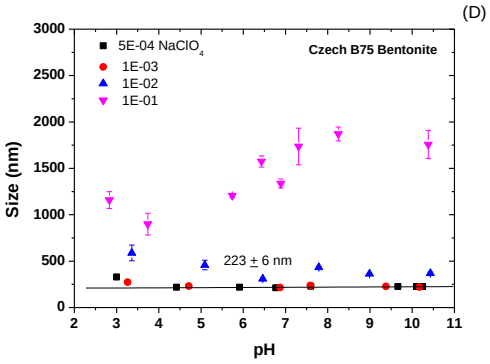
Issue	CIEMAT Outcome
Colloid stability controlling processes	✓ Colloids are stable in low ionic strength waters in absence of bivalent cations.

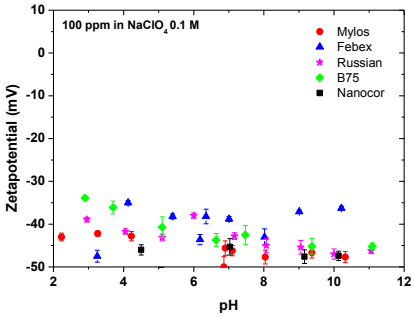


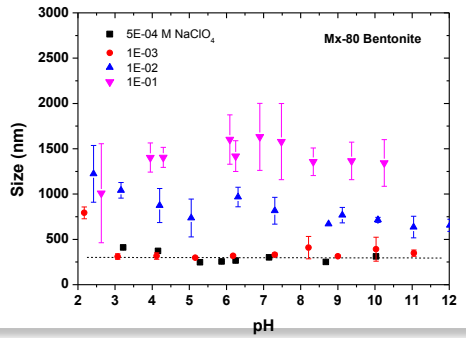
Issue	CIEMAT Outcome
Characteristics of Bentonite clay • The role of divalent cations (WP2 and WP4). • **The stability of different bentonites** (WP4)	✓ When **colloids are NOT stable = no erosion.** ✓ (WP4) **Analysis of colloid stability (size, charge) does not predict erosion behaviour.**

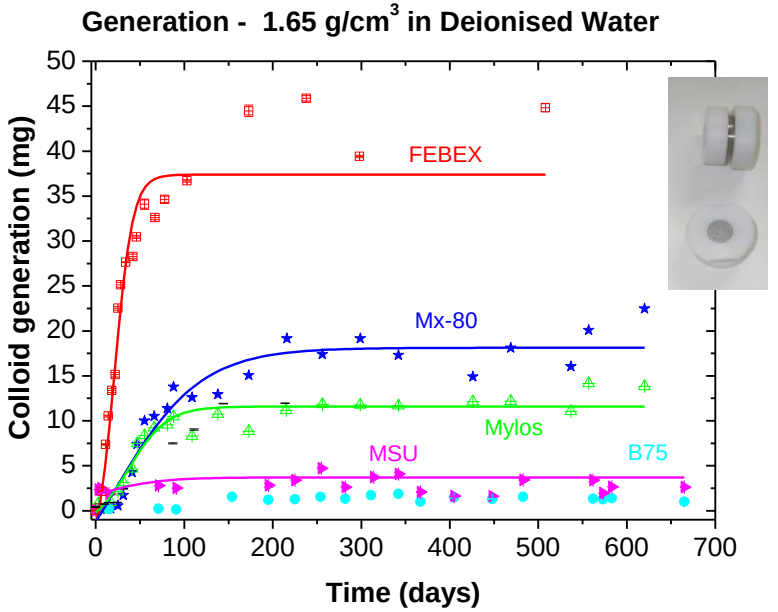


Colloid stability









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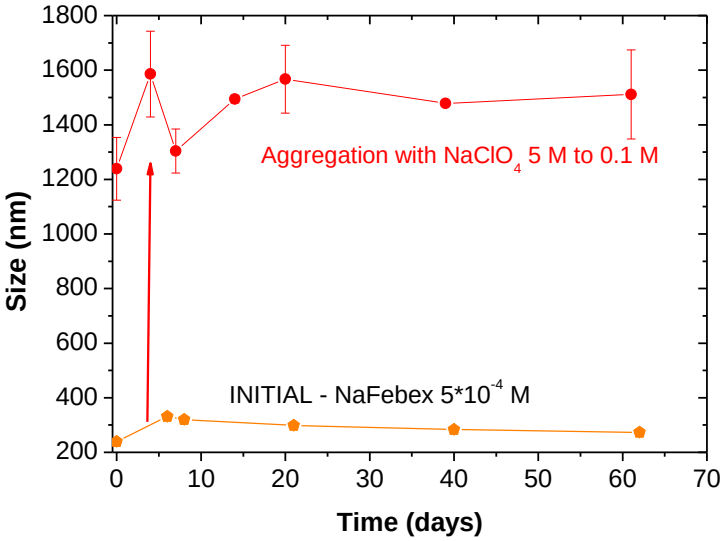
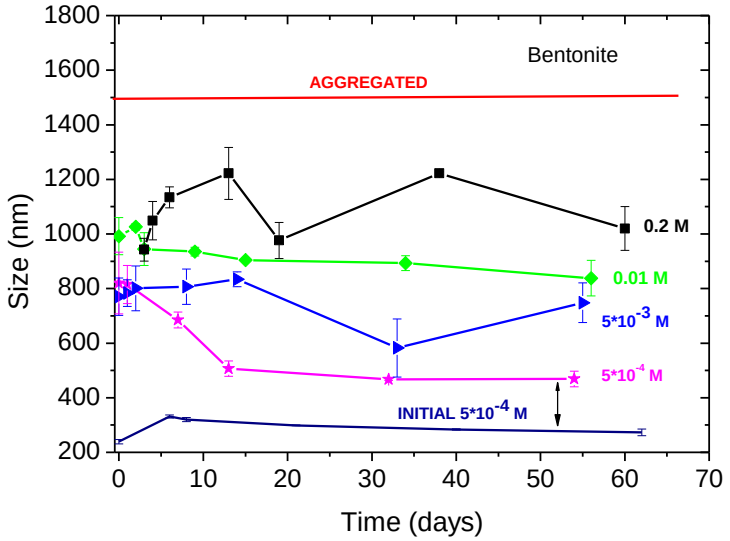
Issue	CIEMAT Outcome: (ir)reversibility
Colloid stability controlling processes • **(Ir)reversibility**	✓ Once colloids are aggregated by decreasing ionic strength initial stable size is not recovered. ✓ Hysteresis ✓ Long-term: scenario evolution

(1) Aggregation



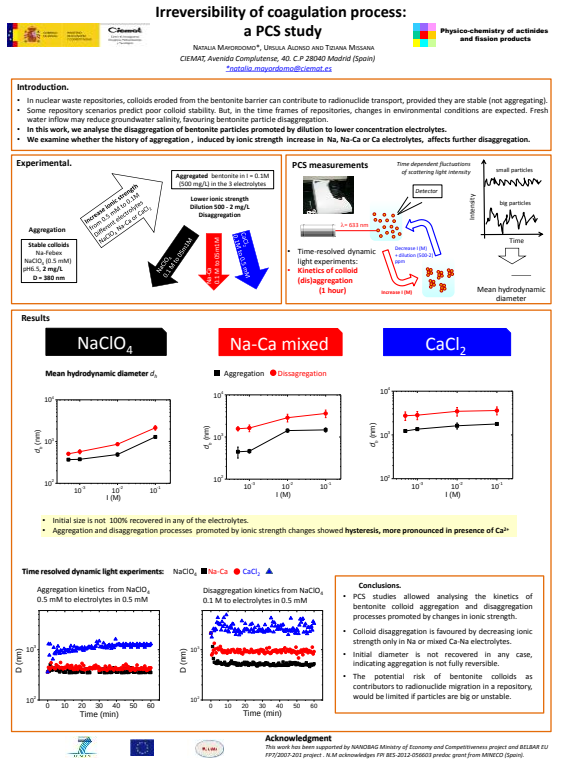
(2) Des-aggregation (dialysis)



Issue	CIEMAT Outcome: (ir)reversibility
Colloid stability controlling processes	✓ Once colloids are aggregated by decreasing ionic strength initial stable size is not recovered.

Poster presentation: Training Course

Natalia Mayordomo



Irreversibility of coagulation process: a PCS study

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Physico-chemistry of actinides and fission products

Introduction.

- In nuclear waste repositories, colloids eroded from the bentonite barrier can contribute to radionuclide transport, provided they are stable (not aggregating).
- Some repository scenarios predict poor colloid stability. But, in the time frames of repositories, changes in environmental conditions are expected. Fresh water inflow may reduce groundwater salinity, favouring bentonite particle disaggregation.
- **In this work, we analyse the disaggregation of bentonite particles promoted by dilution to lower concentration electrolytes.**
- **We examine whether the history of aggregation , induced by ionic strength increase in Na, Na-Ca or Ca electrolytes, affects further disaggregation.**

Experimental.

Aggregation

Stable colloids
Na-Febex
$NaClO_4$ (0.5 mM)
pH≈ 5, 2 mg/L
D ≈ 380 nm

Increase ionic strength (from 0 mM to 0.5 M) (diffferent electrolytes: $NaClO_4$, Na-Ca or $CaCl_2$)

Aggregated bentonite in I = 0.5M (500 mg/L) in the 3 electrolytes

Lower ionic strength
Dilution 500 - 2 mg/L
Disaggregation

PCS measurements

Time dependent fluctuations of scattering light intensity

Detector

λ= 633 nm

- Time-resolved dynamic light experiments:
- **Kinetics of colloid (dis)aggregation (1 hour)**

Decrease I (M) = dilution (500 → 2 ppm

Increase I (M)

small particles

big particles

Intensity

Time

Mean hydrodynamic diameter

Results

$NaClO_4$ | Na-Ca mixed | $CaCl_2$

Mean hydrodynamic diameter d_h

■ Aggregation ● Disaggregation

d_h (nm)

I (M)

- Initial size is not 100% recovered in any of the electrolytes.
- Aggregation and disaggregation processes promoted by ionic strength changes showed **hysteresis, more pronounced in presence of Ca^{2+}**

Time resolved dynamic light experiments: $NaClO_4$ ■ Na-Ca ● $CaCl_2$ ▲

Aggregation kinetics from $NaClO_4$ 0.5 mM to electrolytes in 0.5 mM

Disaggregation kinetics from $NaClO_4$ 0.1 M to electrolytes in 0.5 mM

D (nm)

Time (min)

Conclusions.

- PCS studies allowed analysing the kinetics of bentonite colloid aggregation and disaggregation processes promoted by changes in ionic strength.
- Colloid disaggregation is favoured by decreasing ionic strength only in Na or mixed Ca-Na electrolytes.
- Initial diameter is not recovered in any case, indicating aggregation is not fully reversible.
- The potential risk of bentonite colloids as contributors to radionuclide migration in a repository, would be limited if particles are big or unstable.

Acknowledgment

This work has been supported by NANOBAG Ministry of Economy and Competitiveness project and BELBAR EU FP7/2007-201 project . N.M acknowledges FPI BES-2012-056603 predoc grant from MINECO (Spain).

Issue	Safety case position at start of BELBaR	Outcome
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.*	Understanding of the processes controlling colloid stability and their representation in the safety case (WP4).  WP3

Issue

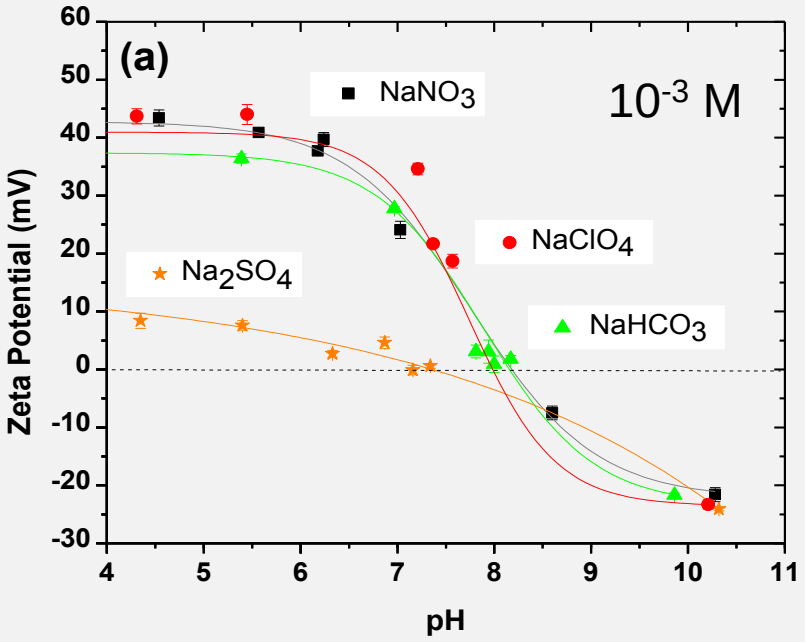
Influence of other factors to colloid stability

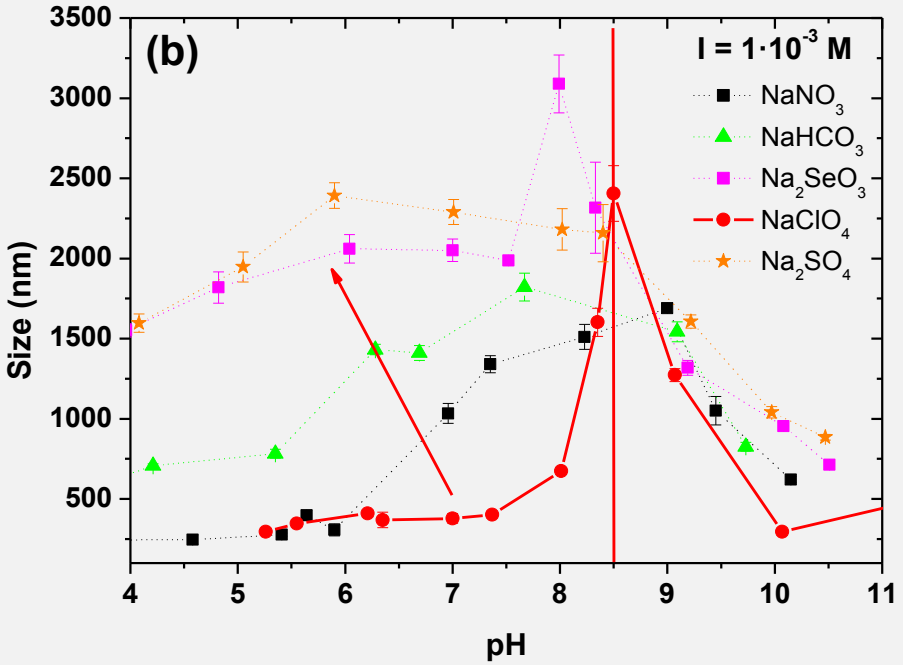
Association of inorganic particles *with natural organic compounds is an important mechanism for* ***colloid stabilisation.***

- **Colloid destabilisation**

CIEMAT Outcome

✓ **Anions present in groundwaters affect** colloids stability





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Issue

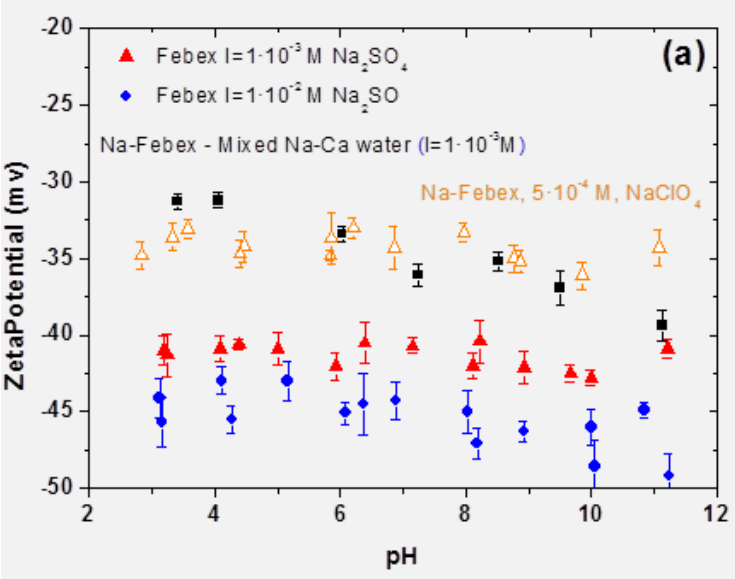
Influence of other factors to colloid stability

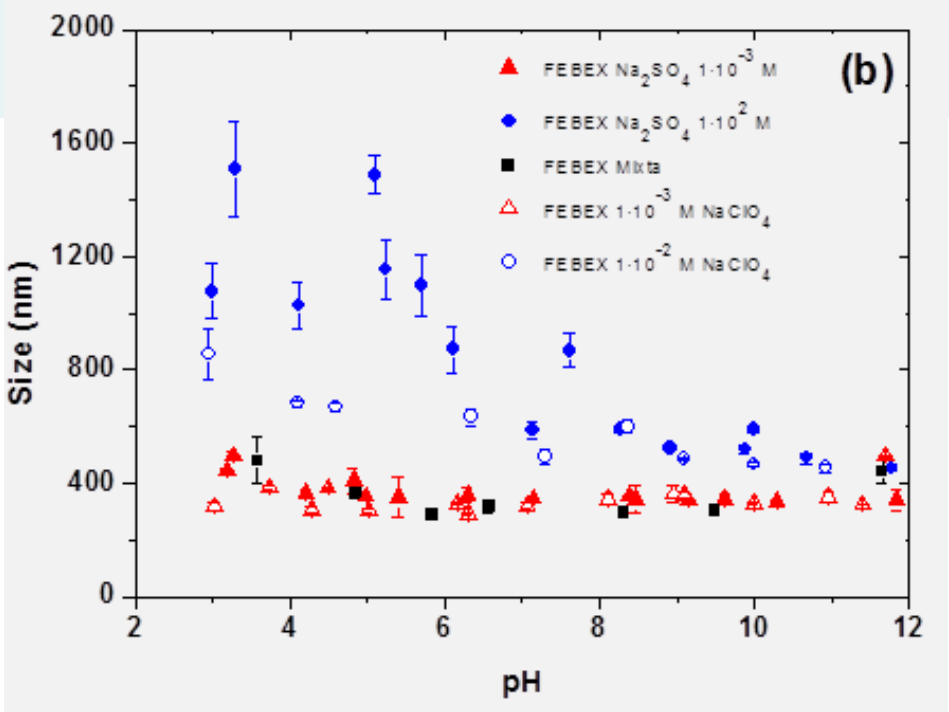
Association of inorganic particles *with natural organic compounds is an important mechanism for* ***colloid stabilisation.***

- **Colloid destabilisation**

CIEMAT Outcome

✓ **Anions present in groundwater affect** bentonite colloids stability





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Issue

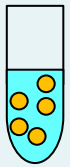
Influence of other factors to colloid stability

Association of inorganic particles *with natural organic compounds is an important mechanism for* ***colloid stabilisation.***

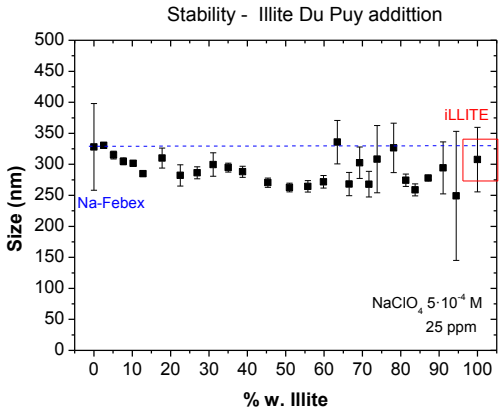
- **Colloid destabilisation**

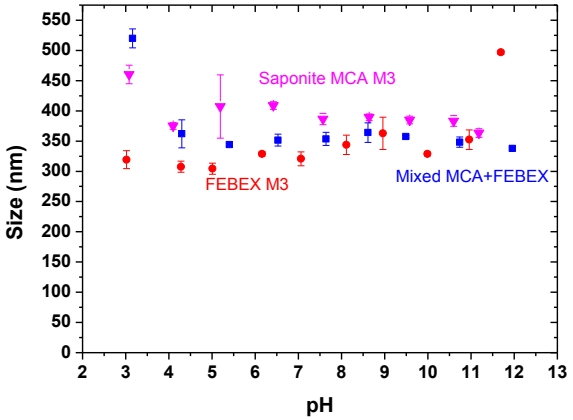
CIEMAT Outcome

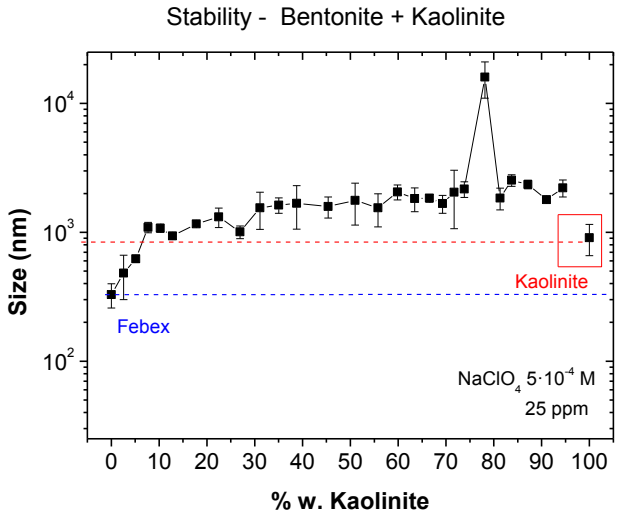
✓ **Mixtures of clays**: some clays destabilised bentonite colloids



Colloid stability



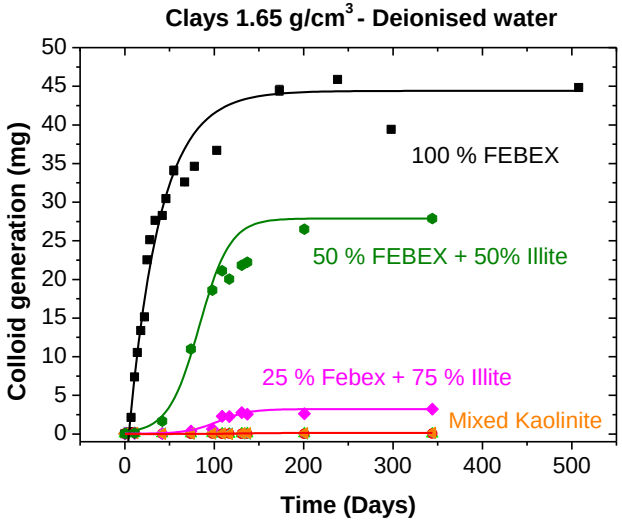




Kaolinite affects bentonite colloid stability

Issue	CIEMAT Outcome
Influence of other factors to colloid stability ***Association of inorganic particles*** *with natural organic compounds is an important mechanism for* ***colloid stabilisation.*** • **Colloid destabilisation**	✓ **Colloid destabilization implies lower erosion** ✓ (WP2) Clay mineralogical compositions and structural characteristics are relevant to define erosion behaviour.

Clay mixtures



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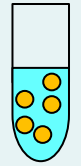
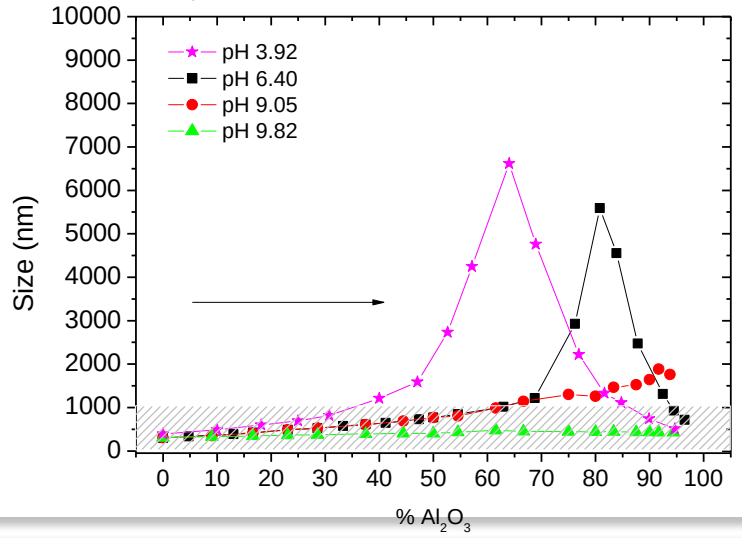
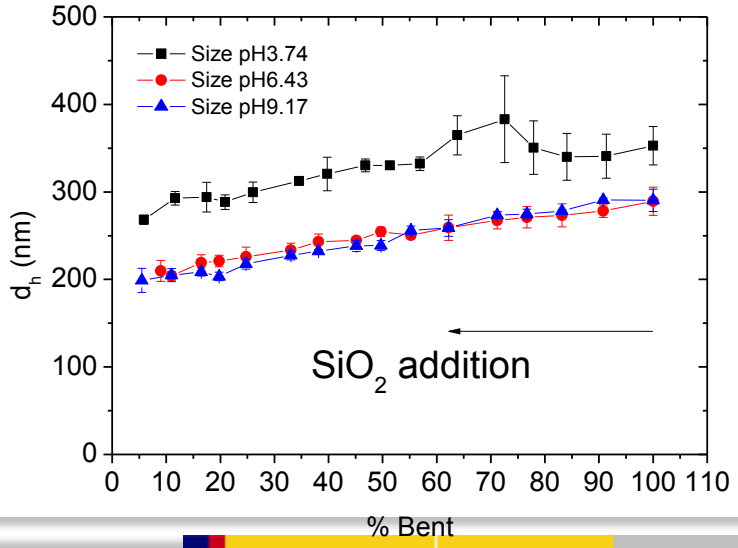
Issue	CIEMAT Outcome
Influence of other factors to colloid stability ***Association of inorganic particles*** *with natural organic compounds is an important mechanism for* ***colloid stabilisation.*** • **Colloid destabilisation**	✓ **Some oxides affect bentonite colloid stability.** ✓ Heteroaggregation



Al_2O_3 addition: Heteroaggregation



SiO_2 addition: Stabilisation



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Issue

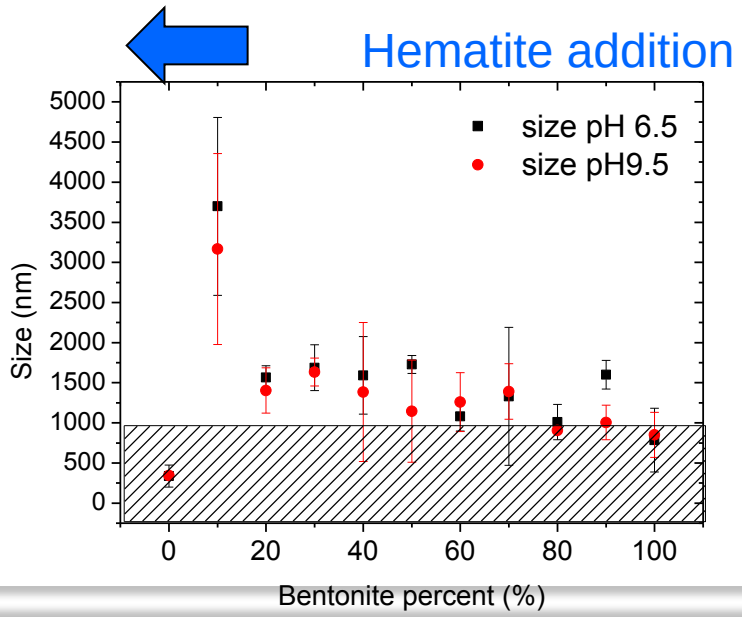
Influence of other factors to colloid stability

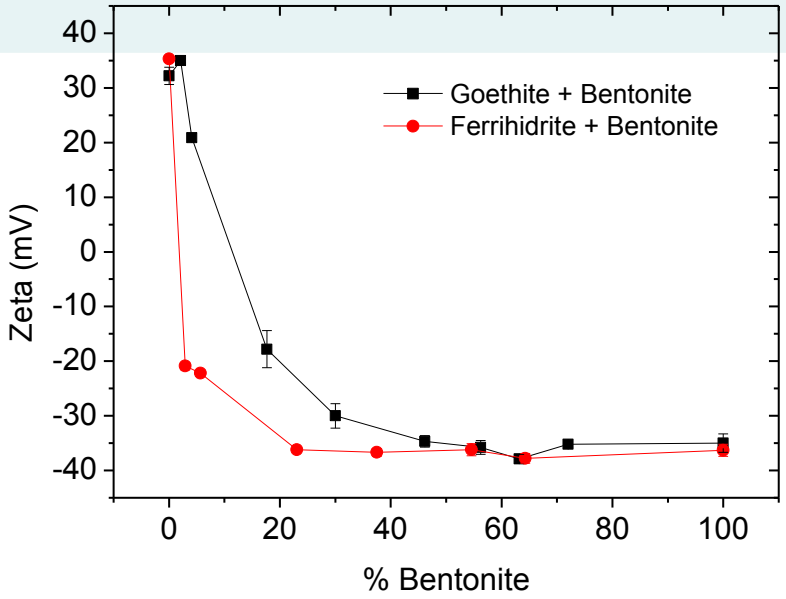
Association of inorganic particles *with natural organic compounds is an important mechanism for* ***colloid stabilisation.***

- **Colloid destabilisation**

CIEMAT Outcome

- ✓ Natural clays: **Fe oxides destabilised bentonite colloids.**
- ✓ Heteroaggregation





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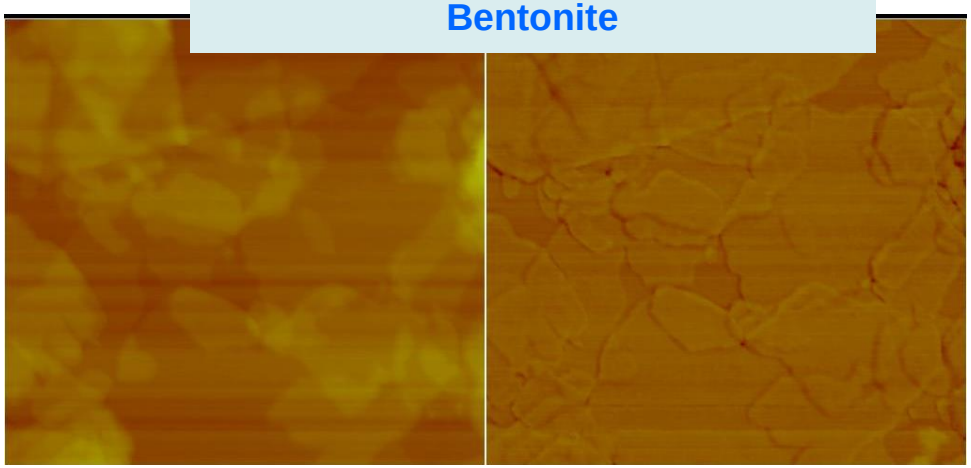
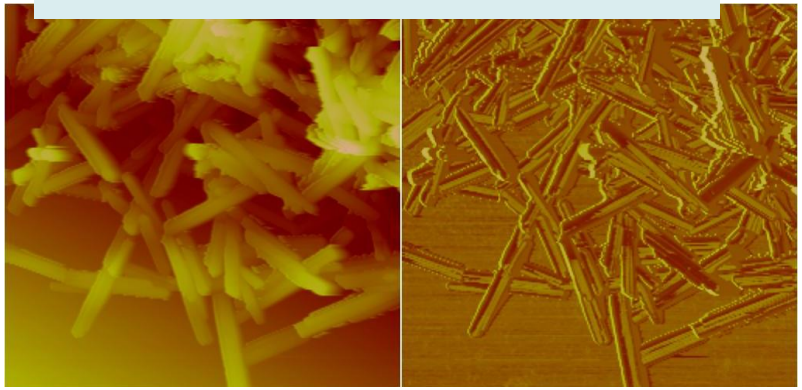
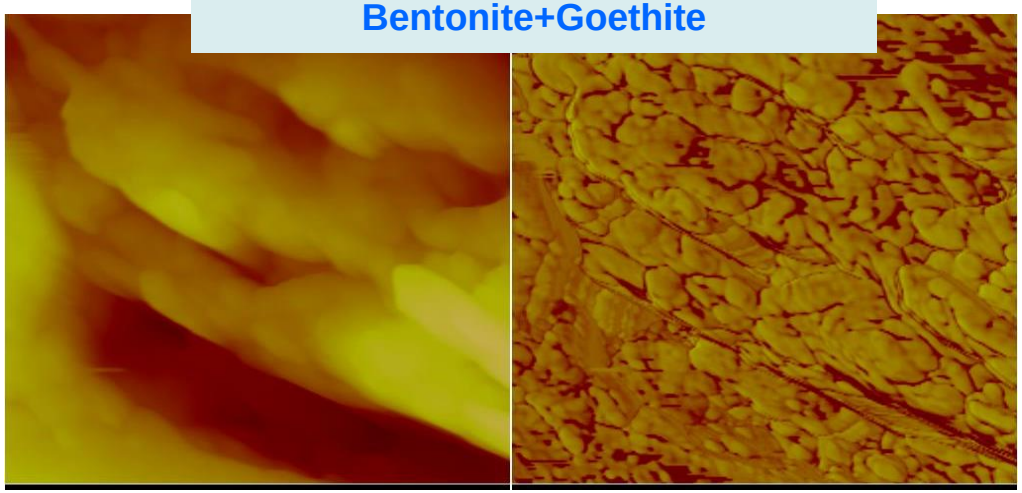
Bentonite



Goethite



Bentonite+Goethite



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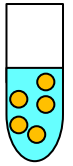
CONCLUSIONS

- **Batch colloid stability analyses do not predict alone bentonite erosion.**
- **Not stable conditions = not erosion.**
- **Some clays and oxides affect bentonite colloid stability.**
- **Clay minerals and oxides are naturally present in raw clays and groundwaters.**
- **<u>For clay mixtures</u>: Clays affecting bentonite colloid stability, affected bentonite erosion.**
- **Erosion experiments with bentonite mixed with zeolite, saponite and oxides are ongoing.**



Thank you for your attention

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