Destabilization of bentonite colloids by addition of alumina nanoparticles

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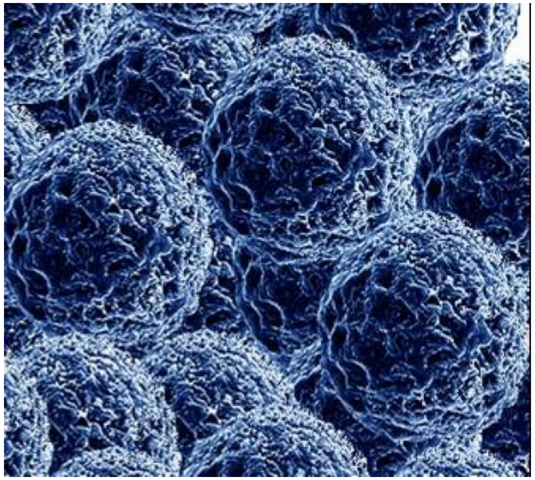
1. Introduction

Why studying the interaction with alumina nanoparticles?



- ↑Surface area/volume
- Ubiquitous in environment at ↑concentration
- Interaction between inorganic colloids

1. Introduction

What would happen if bentonite interacts with alumina nanoparticles ?

Will alumina aggregate or stabilize bentonite suspensions?

How does bentonite-nanoparticle mixture behave in different chemical conditions?

Under which conditions migration will be avoided?

1. Introduction

Materials:

Alumina Nanoparticles:

- ϒ-Al_2O_3
- Nominal size <50 nm
- BET 136 m^2/g

+

Na Bentonite

- FEBEX bentonite
- From Cortijo de Archidona, Almería, Spain
- 93% smectite content
- Other components: 2% quartz, 3% plagioclase, 2% cristobalite and trazes of calcite, feldespar and tridymite
- BET 33 m^2/g

1. Introduction

Methods:

Size

Hydrodynamic diameter

Diffusion Light Scattering techniques

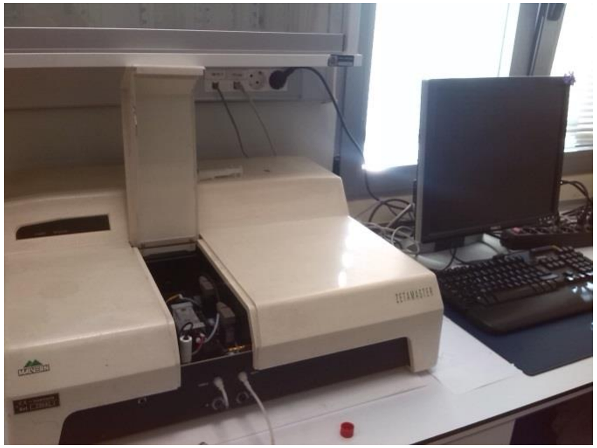
Charge

ζ potencial

Laser Doppler electrophoresis

λ=633 nm

λ= 514nm



λ=633 nm

1. Introduction

Methods:

1. Stability upon pH and I changes

- ✓ Hydrodynamic diameter
- ✓ ζ potencial
- ❑ 100% bentonite
- ❑ 100% alumina
- ❑ Two mixture proportions

2. "Titration" effect of sample proportion

- ✓ Hydrodynamic diameter
- ❑ Addition of well known volumes
- ❑ From 100% to 0% mixture proportion
- ❑ Fixed pH
- ❑ $5 \cdot 10^{-4}$M

3. Kinetics

- ✓ Size and charge changes on time
- ❑ Fast aggregation kinetics in 60 min

4. Characterization

- ✓ Infrared spectra
- ✓ Atomic Force Microscopy
- ✓ Scanning Electron Microscopy

2. Results: stability

Stability studies

- **ζ-potential** using Zetamaster Malvern
- **Hydrodynamic diameter** using Malvern 4700C and Malvern Nano ZS
- Δ pH (3->11)
- Δ I using $NaClO_4$ ($5 \cdot 10^{-4}$-> 0.1) M

- Independent

  100% Al_2O_3

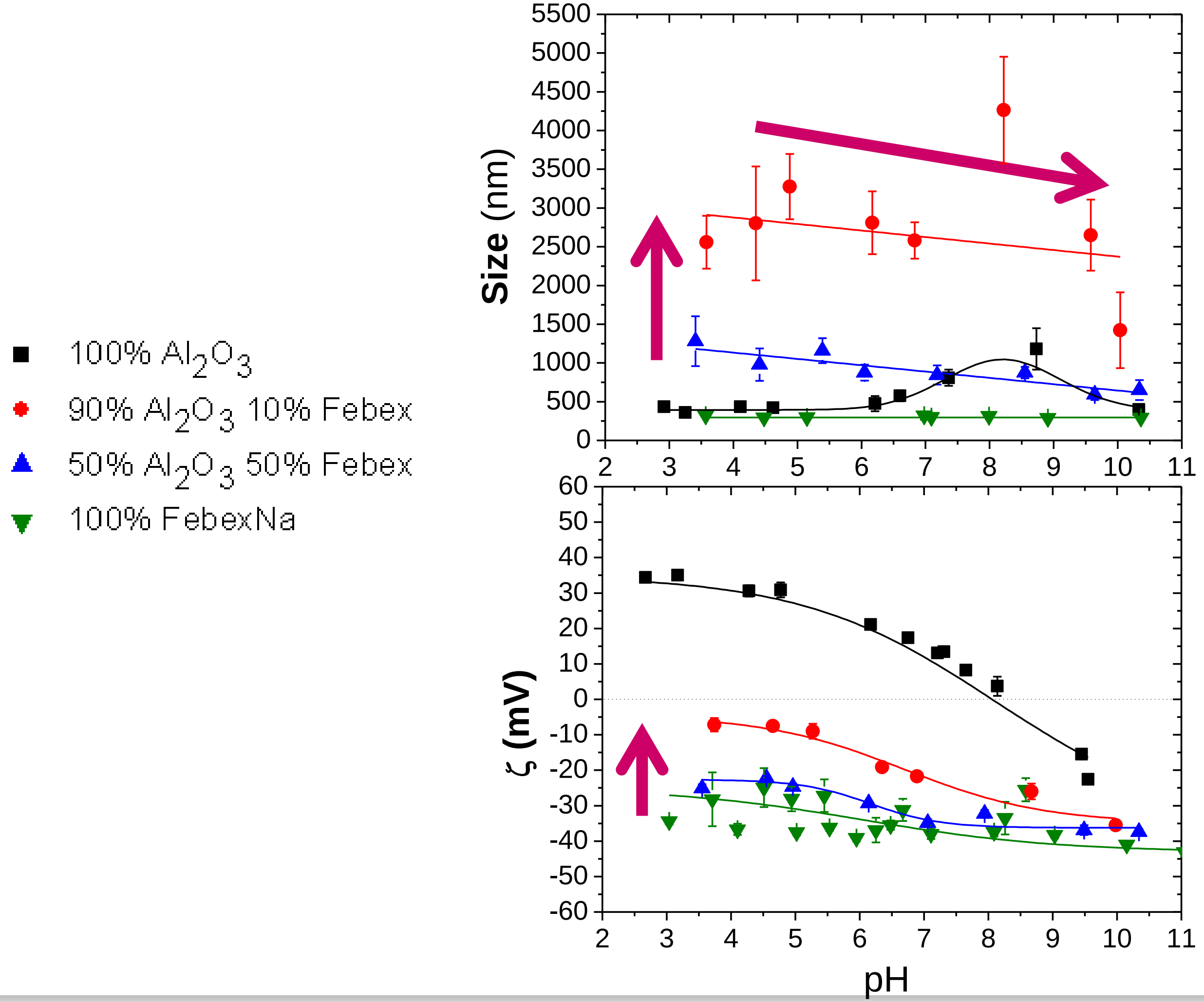
  100% NaBentonite
- Mixtures Al_2O_3/NaBentonite weight proportions:

  50Al_2O_3/50NaBentonite

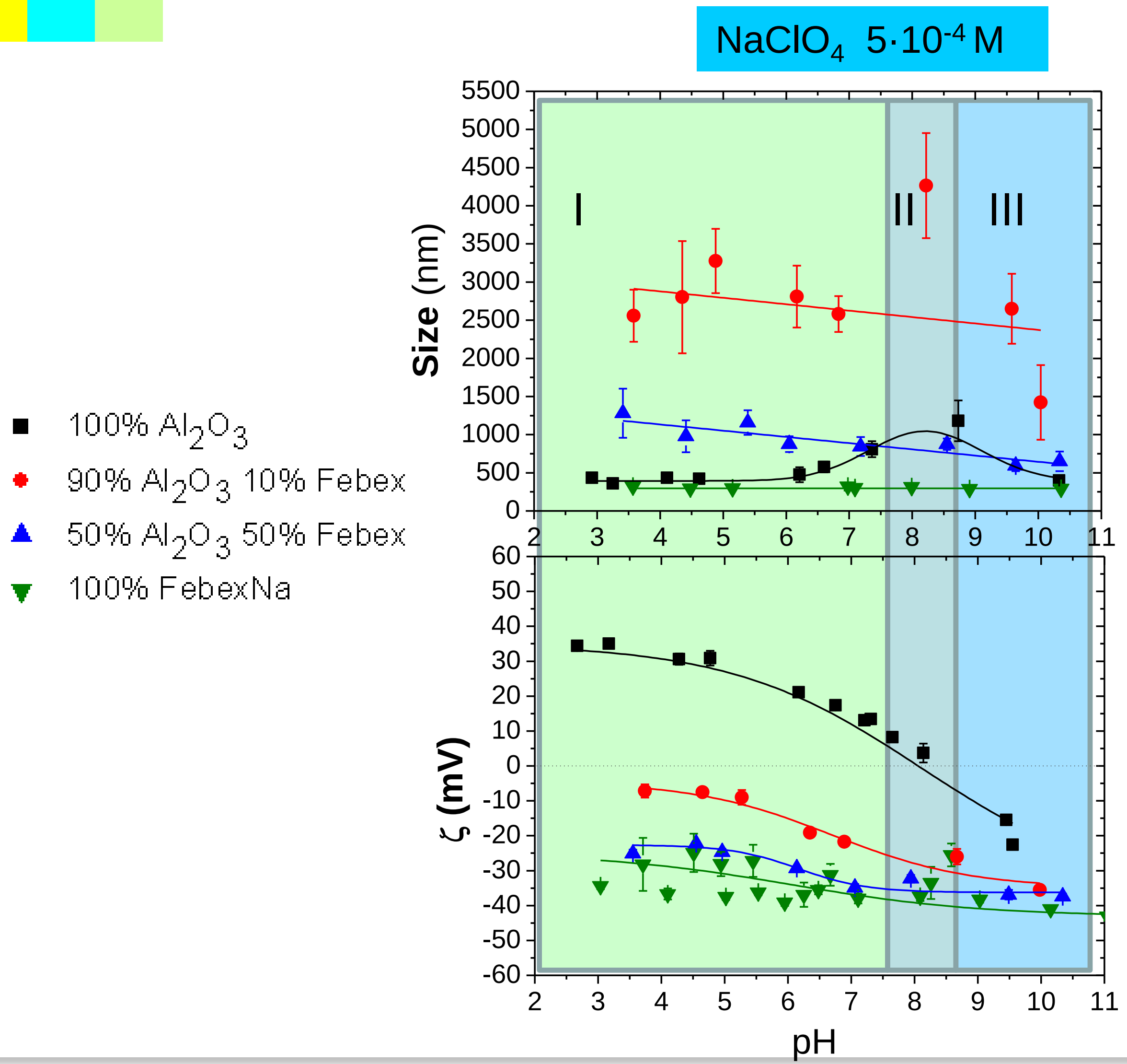
  90Al_2O_3/10NaBentonite
- Total concentration 10 mg/L

2. Results: stability

$NaClO_4$ $5\cdot10^{-4}$ M



2. Results: titrations



- Hydrodynamic diameter with changing % of mixture
- Fast titrations
- Fixed pH
- I = 5·10^{-4} M
- Adding 500 mg/L aliquots

Areas:

- Area I- pH<pH 7

Alumina δ+, bentonite δ-

- Area II- pH≈pH zpc

Aluminaδ0, bentonite δ-

- Area III- pH>9

Aluminaδ-, bentonite δ-

2. Results: “titrations”

Size measurements

100% Bentonite
500 mg/L

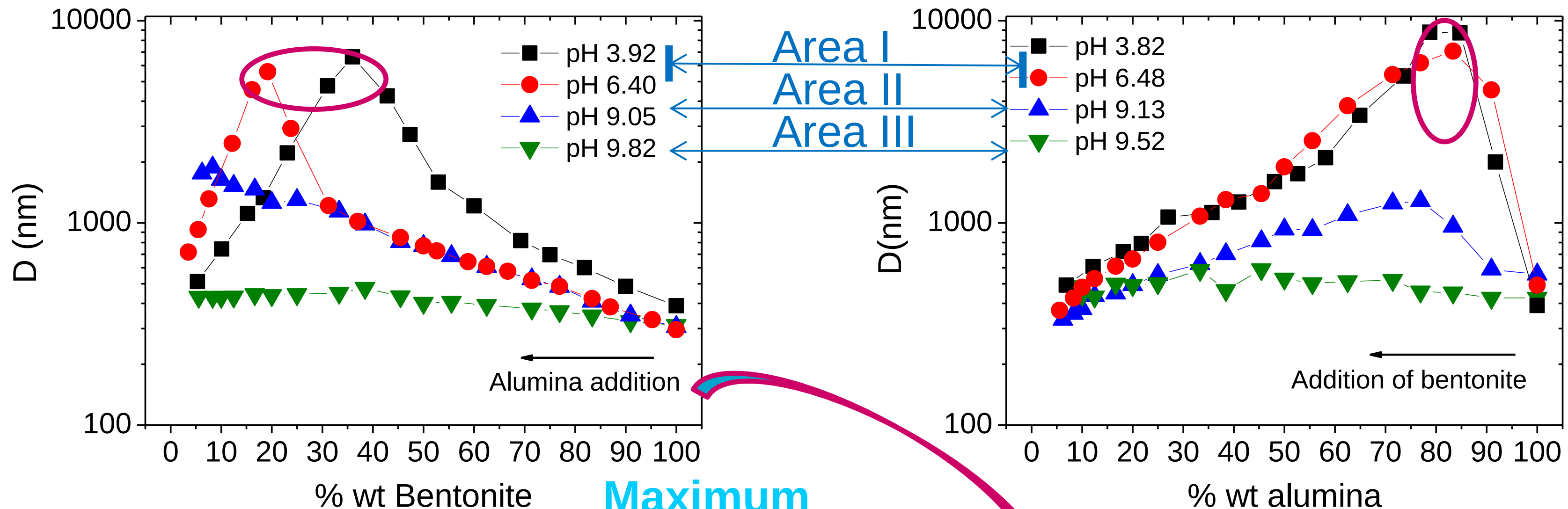
100% Alumina
500 mg/L

pH and conductivity controlled during the experiment in both beakers

2. Results: titrations

Bentonite upon alumina addition

Alumina upon bentonite addition



Maximum 80%Alu. - 20%Bent.

Areas I & II
- ↑Heteroaggregation ↑%Alumina
- ↑Heteroagregation ↓pH
- ≈50% alumina destabilization complete
- **Maximum at a fixed mixture proportion**

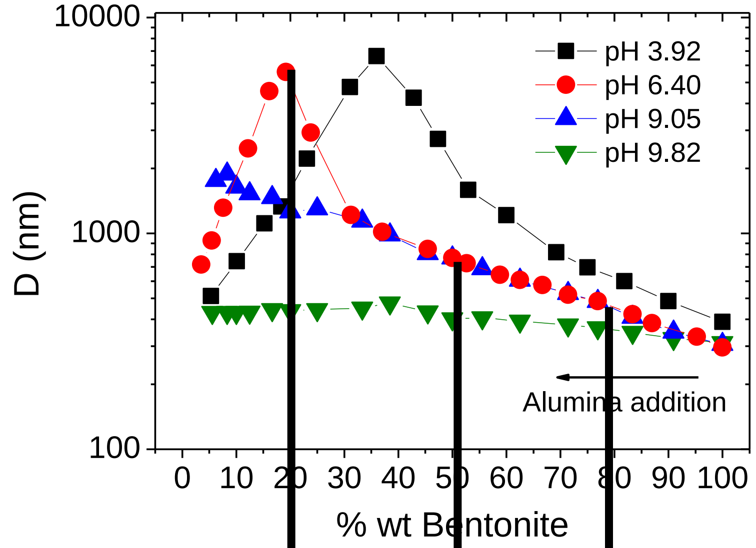
Area III
- ↑Alumina content does not destabilize mixtures size ≈400nm

pH	D_0	D_f
3.92	485	513
6.40	332	716
9.05	349	1761
9.82	326	430

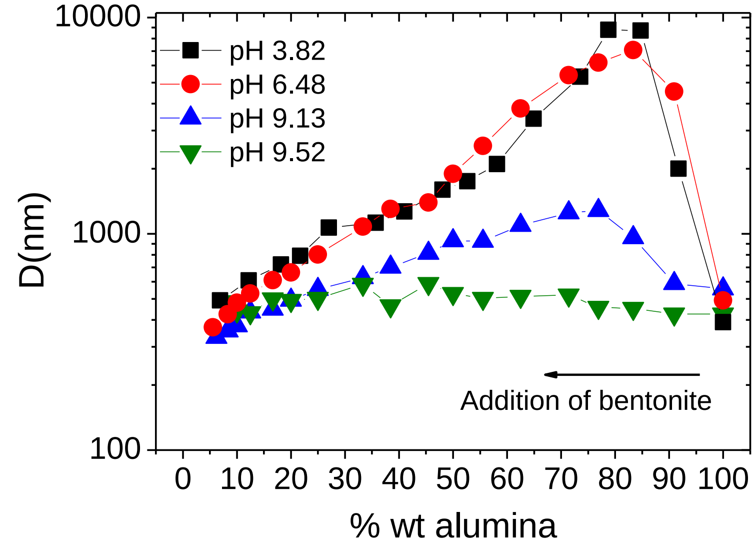
pH	D_0	D_f
3.82	390	492
6.48	492	370
9.13	557	332
9.52	425	484

2. Results: kinetics

Bentonite upon alumina addition



Alumina upon bentonite addition



80%Bentonite 20%Alumina

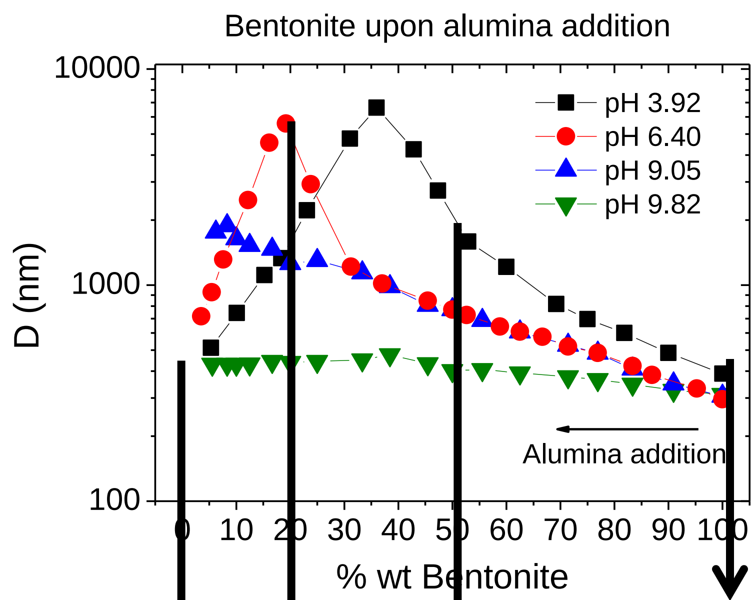
50%Bentonite 50%Alumina

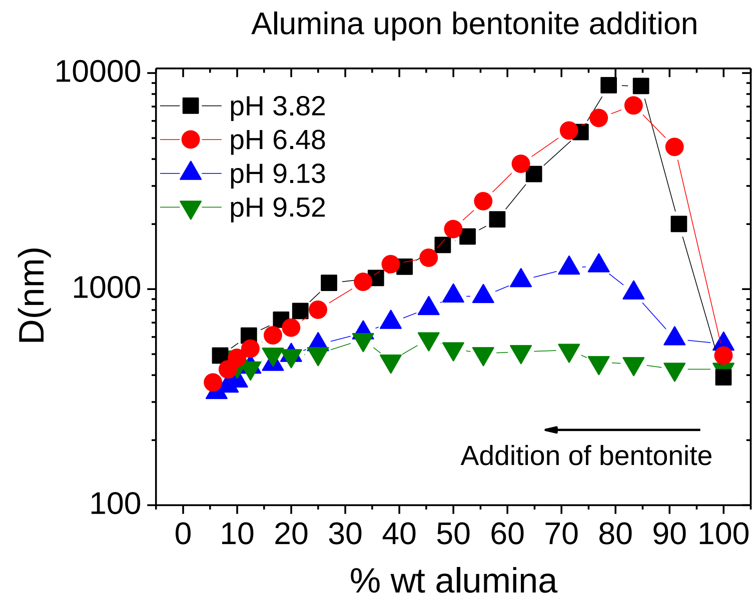
20%Bentonite 80%Alumina

*Stability kinetics

- pH 6.5
- $I = 5\cdot10^{-4}$ M
- t = 30 days
- Size and ζ potencial
- Tot. conc. 500 mg/L

2. Results: kinetics





100%Bentonite

50%Bentonite 50%Alumina

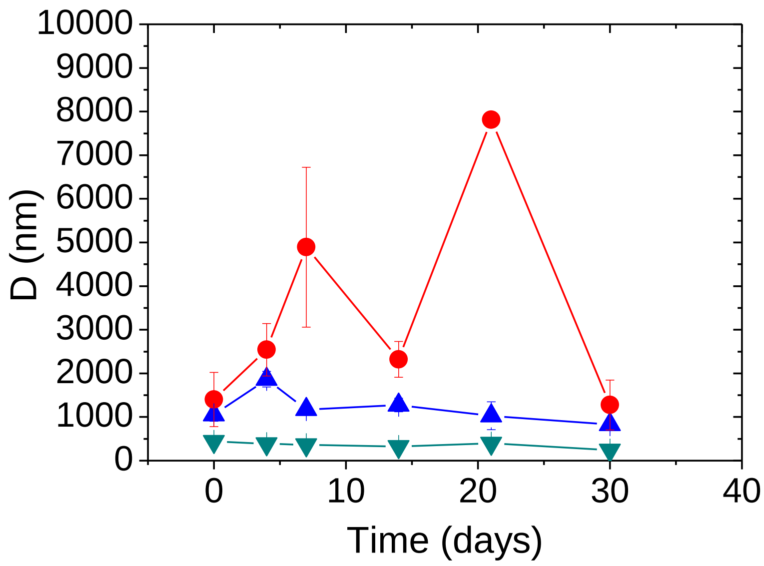
20%Bentonite 80%Alumina

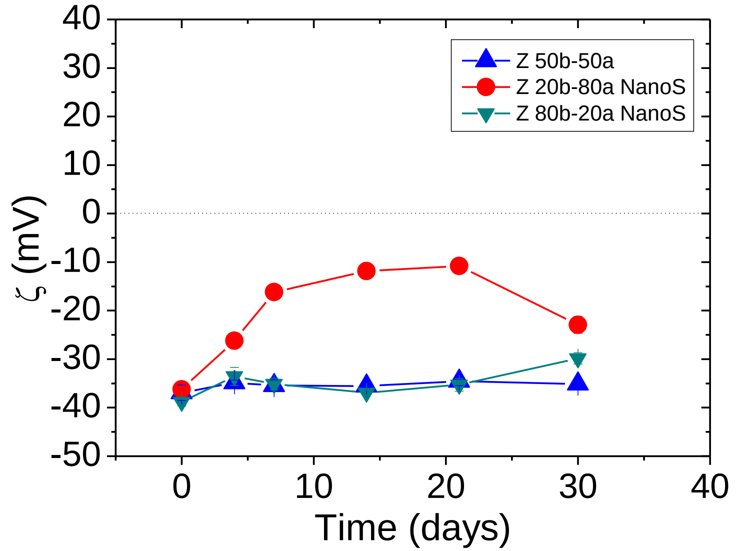
100%Alumina

*Aggregation kinetics

- 60 minutes
- $I = 5\cdot10^{-4}$ M
- ΔpH
- Tot. conc. 500 mg/L

2. Results: kinetics





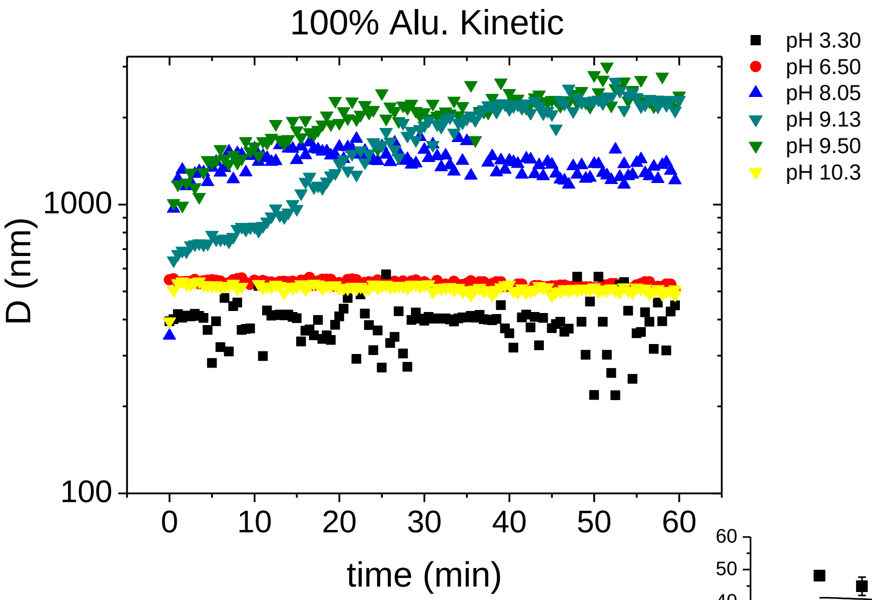
80% Alumina- 20% Bentonite

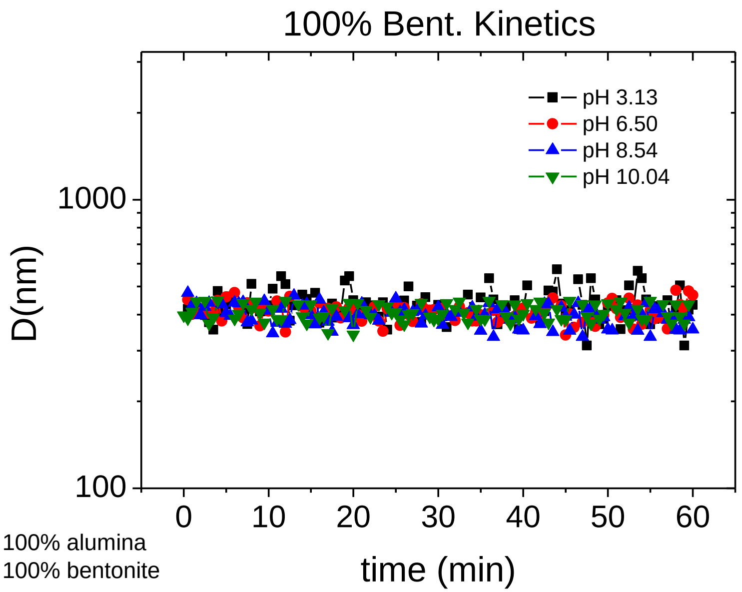
50% Alumina- 50% Bentonite ➤ (1200±350) nm

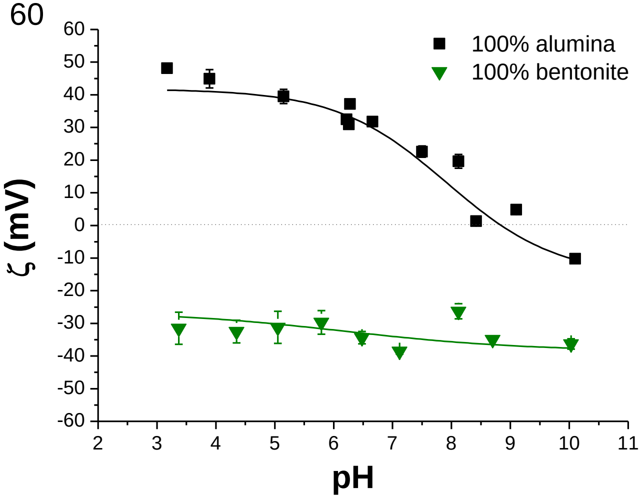
20% Alumina- 80% Bentonite ➤ (357±69) nm

- Mixtures <50% alumina content no relevant changes on size and charge with time
- Unstable maximum 80% alumina content: it remains unstable when passing time, slight increase of zeta potencial with time

2. Results:
aggregation kinetics



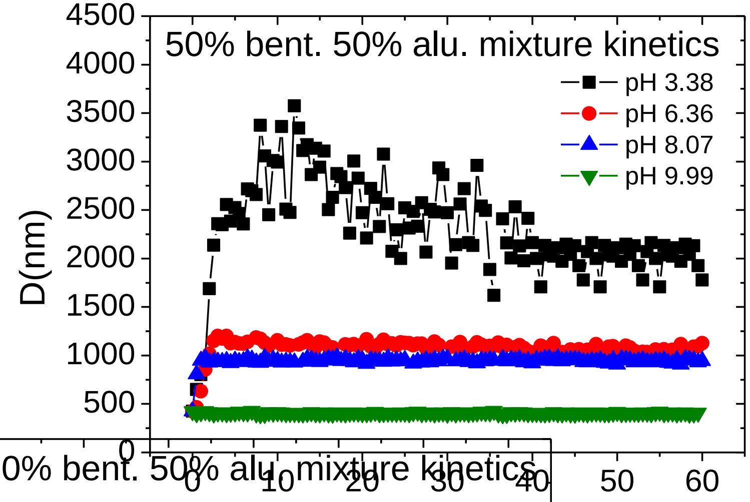


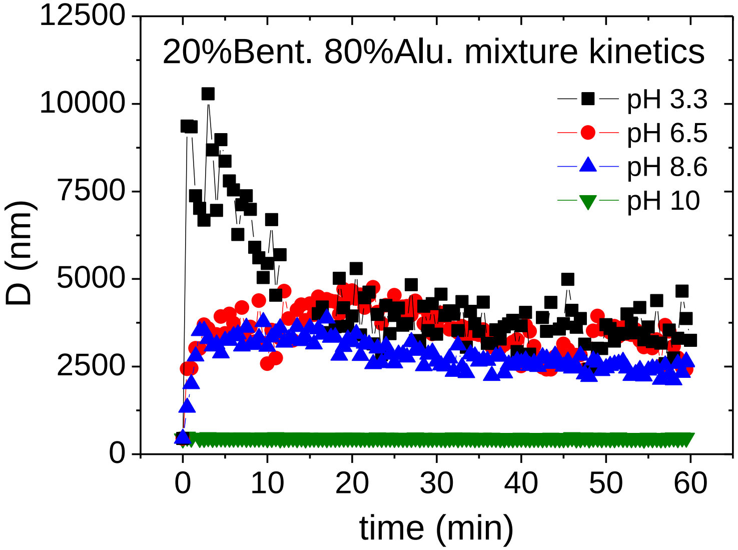


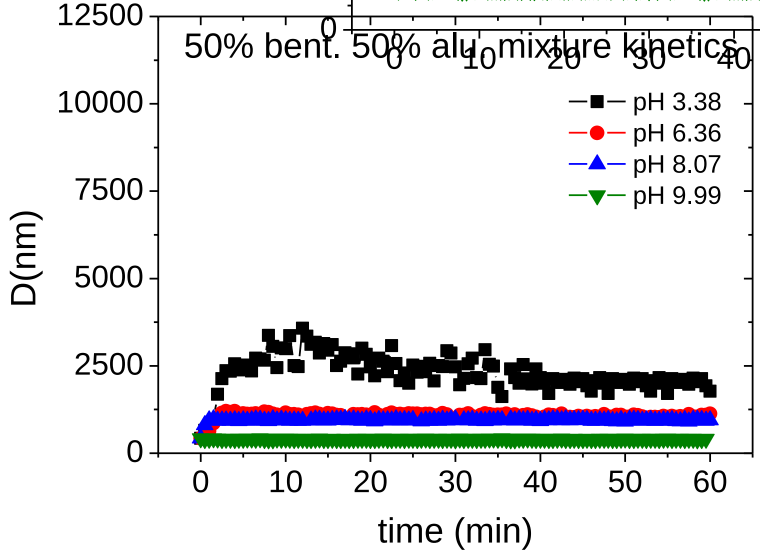
-100% individual systems

2. Results:
aggregation kinetics

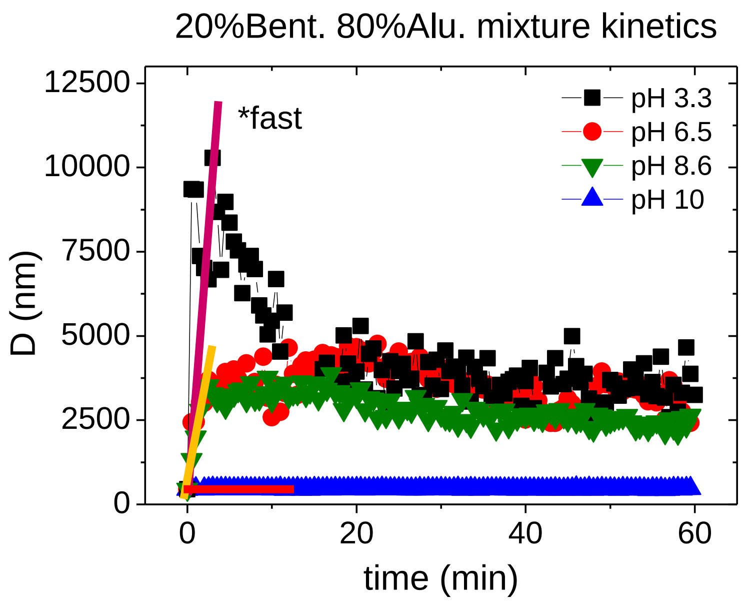
-Mixtures







2. Results:
aggregation kinetics

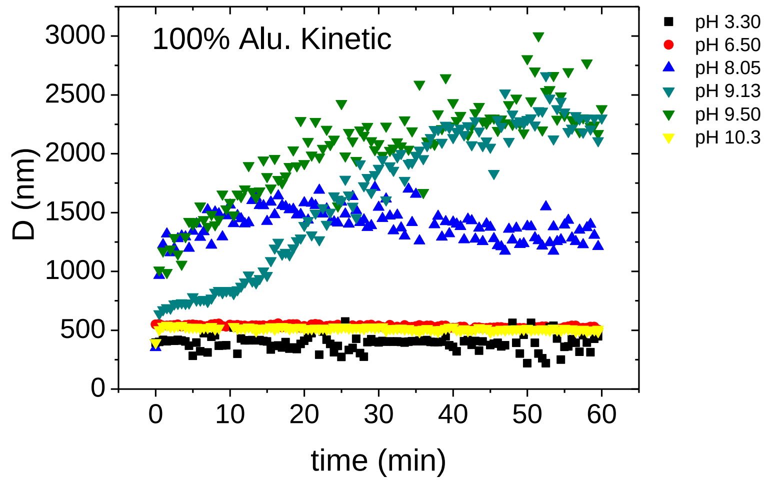


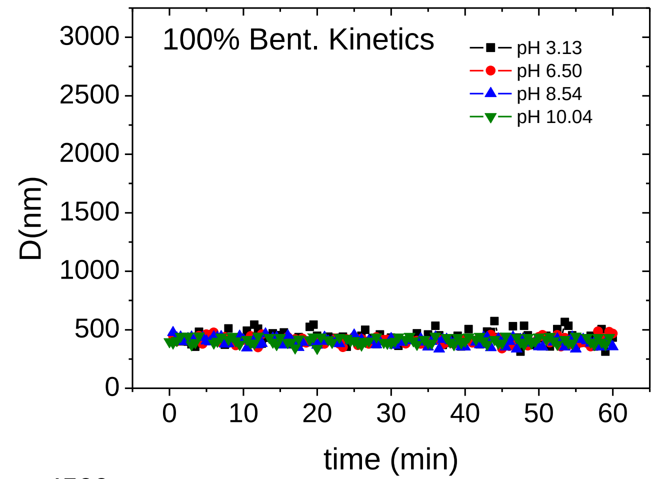
Coagulation efficiency, α

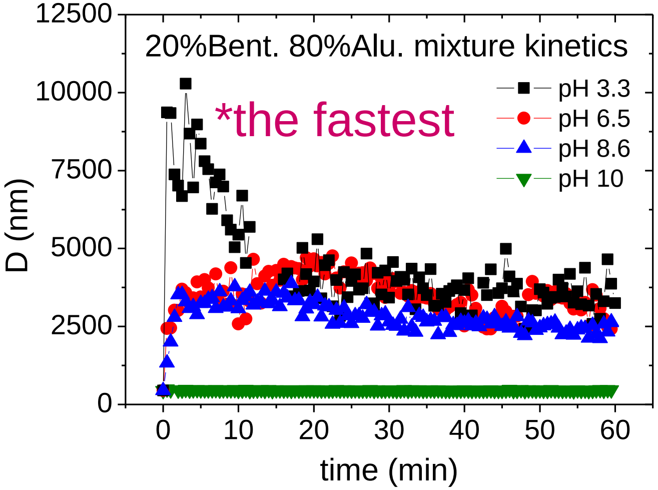
$$\alpha = \frac{1}{W} = \frac{\left(\frac{\delta d_h}{\delta t}\right)_{t\to 0}}{\left(\frac{\delta d_h}{\delta t}\right)_{fast\ coagulation}}$$

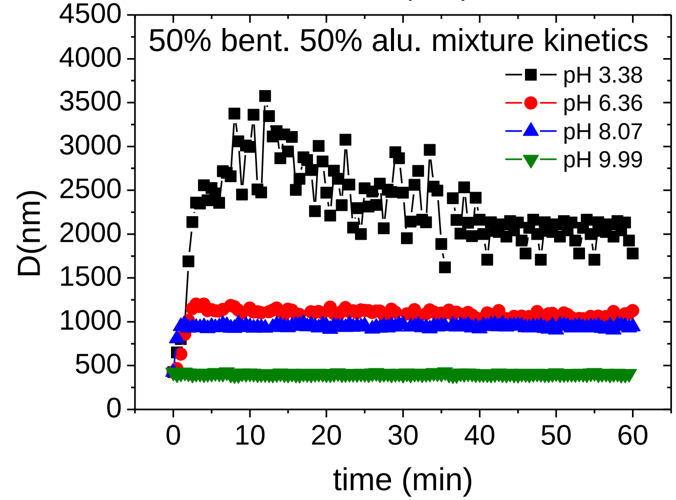
Where,
W is the stability ratio,
$\left(\frac{\delta d_h}{\delta t}\right)_{t\to 0}$ slow (de)coagulation process slope in nm/min
$\left(\frac{\delta d_h}{\delta t}\right)_{fast}$ fast (de)coagulation process slope in nm/min

2. Results: aggregation kinetics

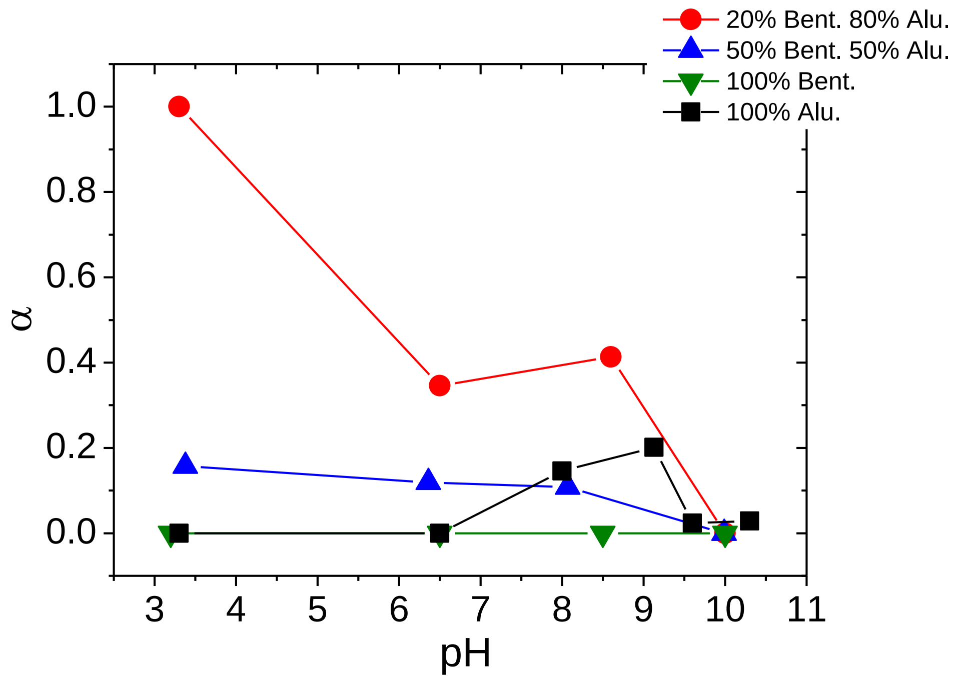






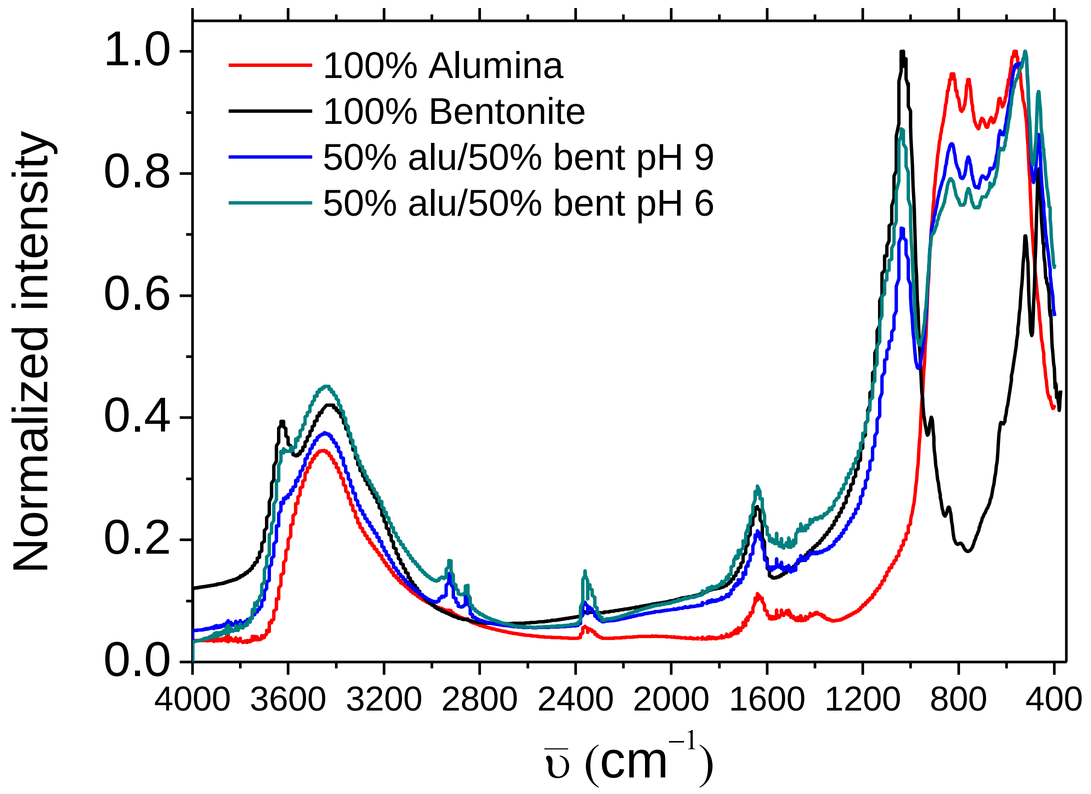


2. Results:
aggregation kinetics

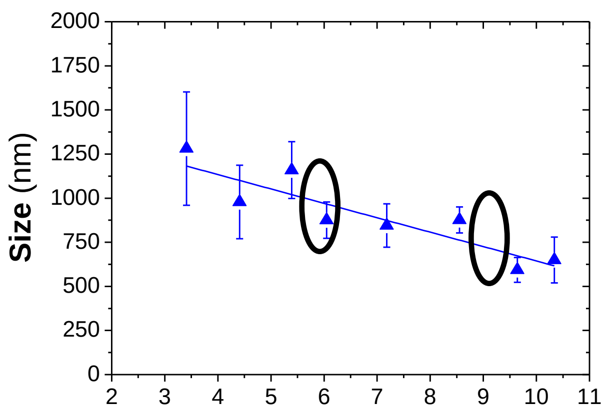


Respecting the fastest aggregation : 20%bent.-80%alu pH3

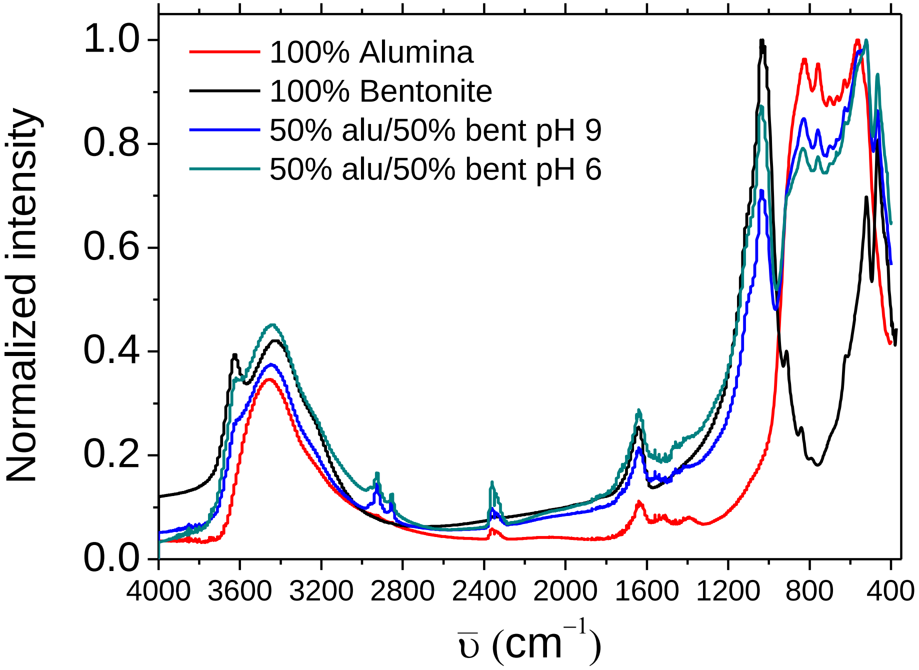
2. Results:
microscopy and infrared



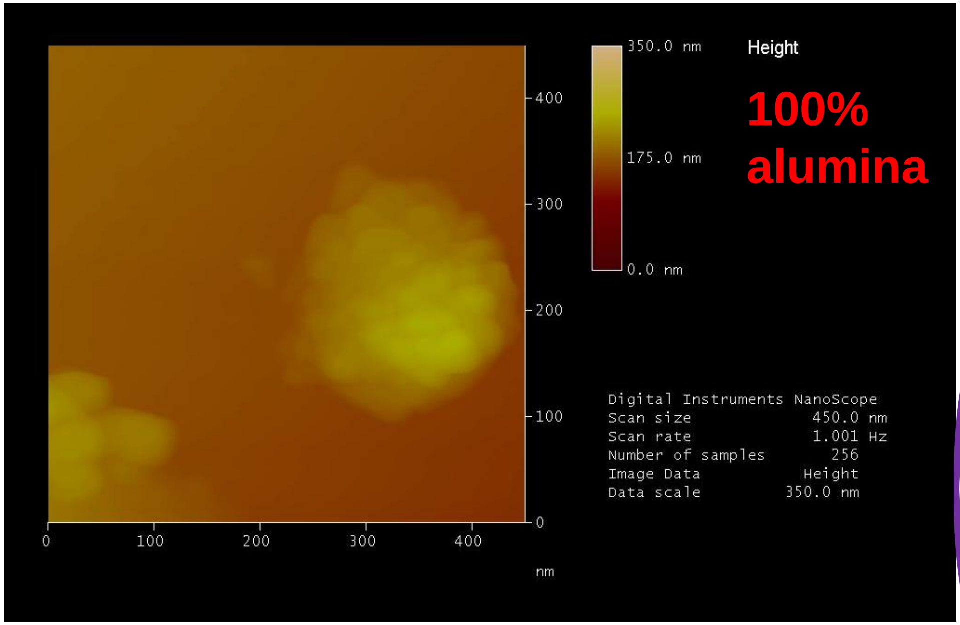
- 7 days interaction
- Total concentration 500 mg/L
- I = 5·10^{-4} M

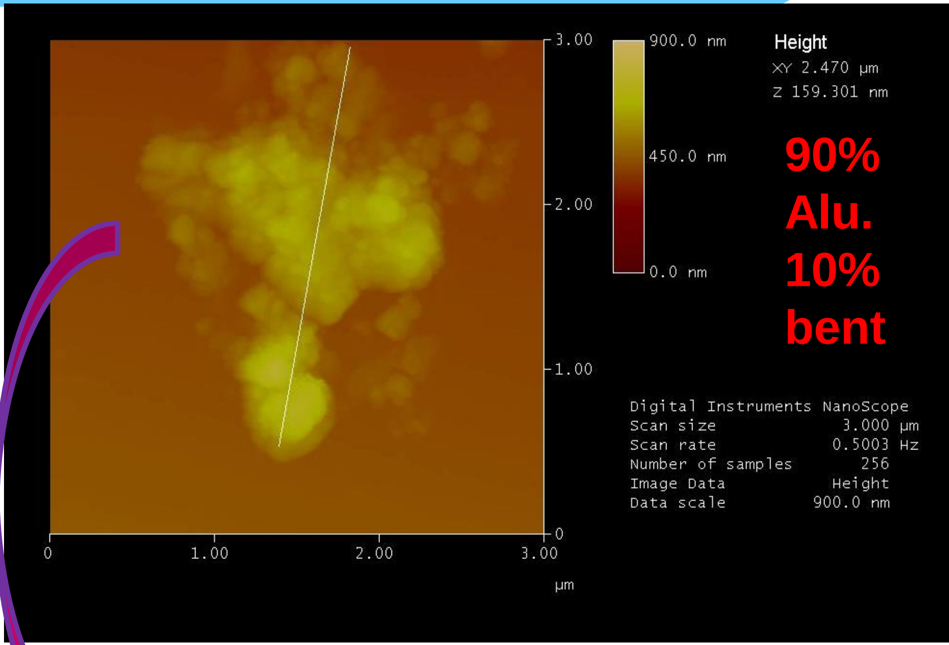


2. Results:
microscopy and infrared



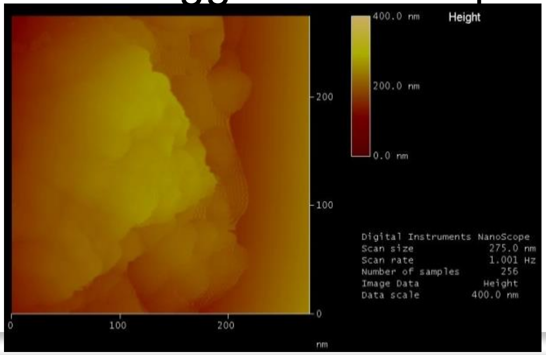
2. Results: microscopy and infrared





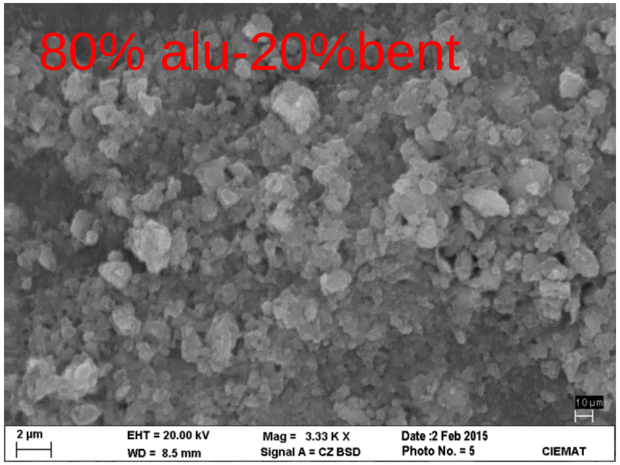
- Homoaggregates ≈250 nm
- Nanoparticles (40-60) nm

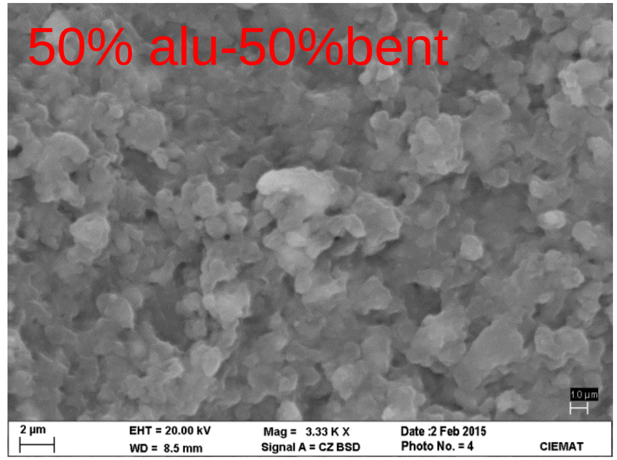
- Heteroaggreates >2.5µm

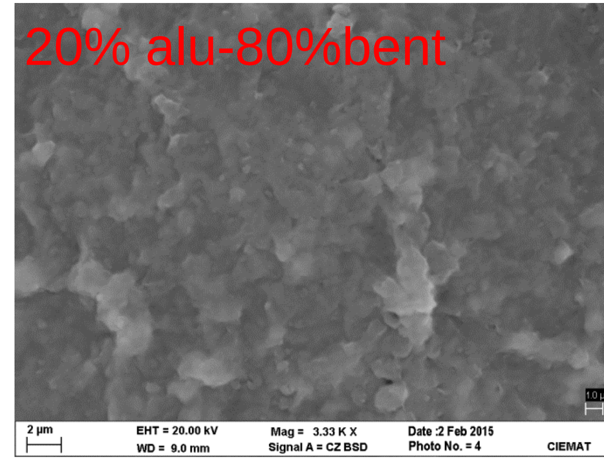


- pH 9
- $I = 5 \cdot 10^{-4}$ M

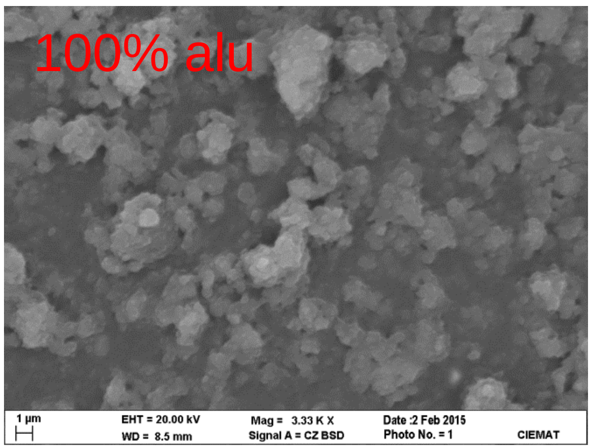
2. Results: microscopy and infrared

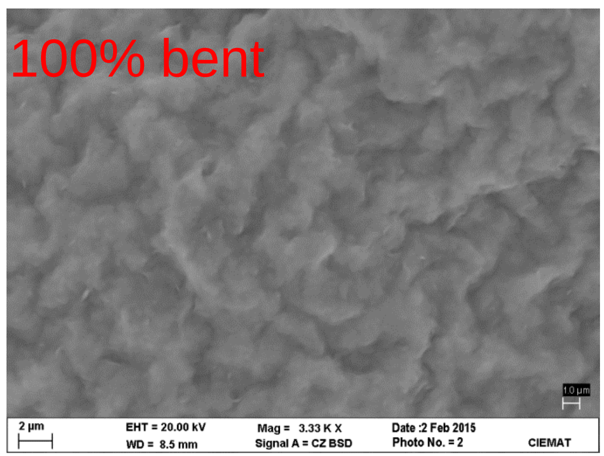






↓Alumina content



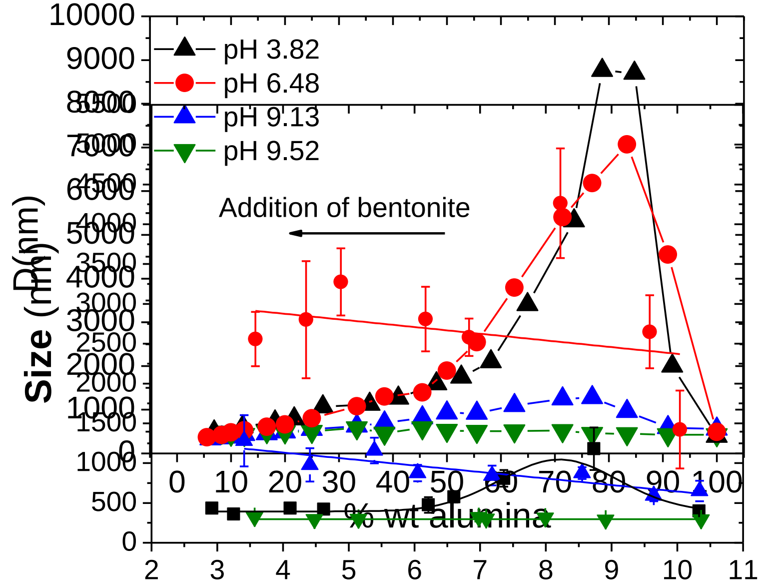


- pH 6.5
- Dried suspension
- Over C
- Total Conc.100 mg/L
- 20kW voltage

3. Conclusions

What would happen if we add alumina nanoparticles to bentonite?

- Addition of alumina, destabilizes bentonite colloids, even at in low alumina proportions at pH<9
- Heteroaggregation is higher at low pH values and higher ionic strengths



Bentonite colloids coming from erosion would aggregate with alumina after which a sedimentation process would occurr.

This would affects colloid migration

4. Acknowledgment

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