WP 4
Subsurface transport of nanoparticles

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NanoRem Final Conference

Nanoremediation for Soil and Groundwater Clean-up
- Possibilities and Future Trends

Frankfurt am Main, 21st November 2016

Some background slides

Factors influencing delivery and subsurface nanoparticles transport

- Injection technique (pressure, velocity, well type, etc.)
- Type of injection suspensions (viscosity, conc., etc.)

- Aquifer material properties (grain size, chemical and physical surface properties and heterogeneity, etc.)
- Aquifer groundwater chemistry (pH, ionic strength, NOM)
- Nanoparticles properties (size, density, concentration, surface properties, etc.)

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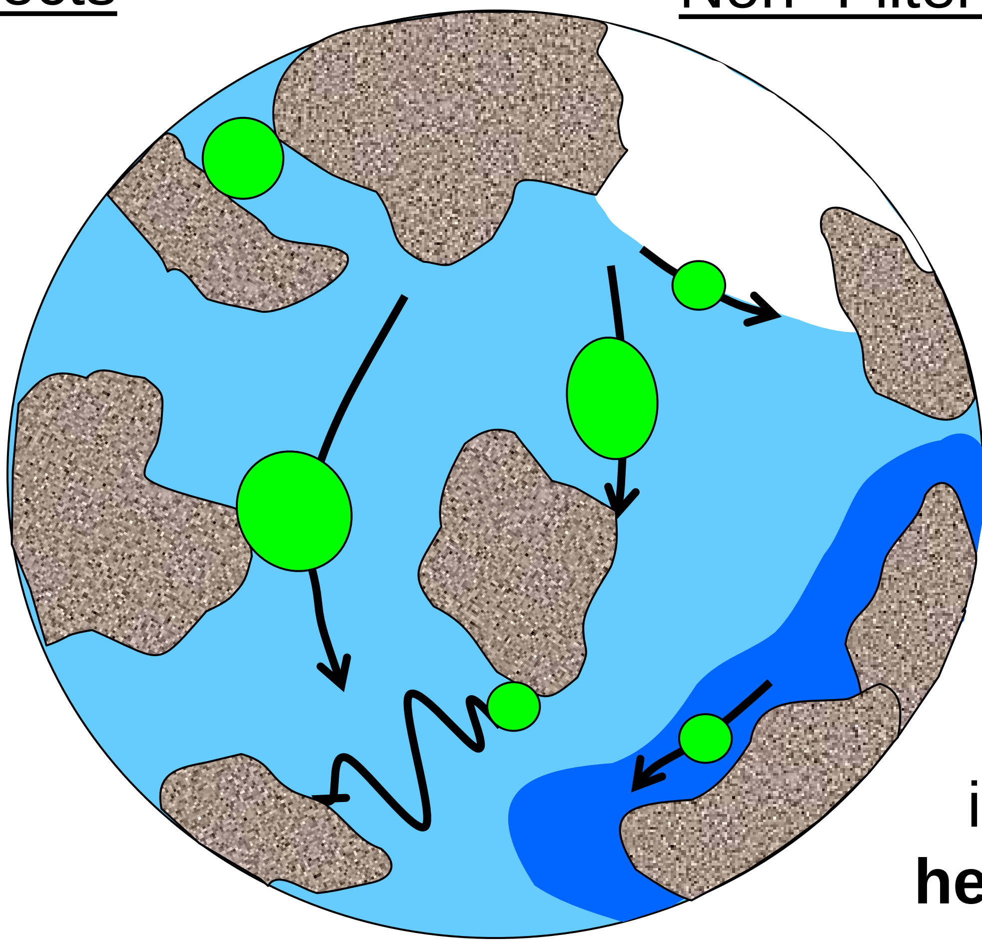
Particle Filtration



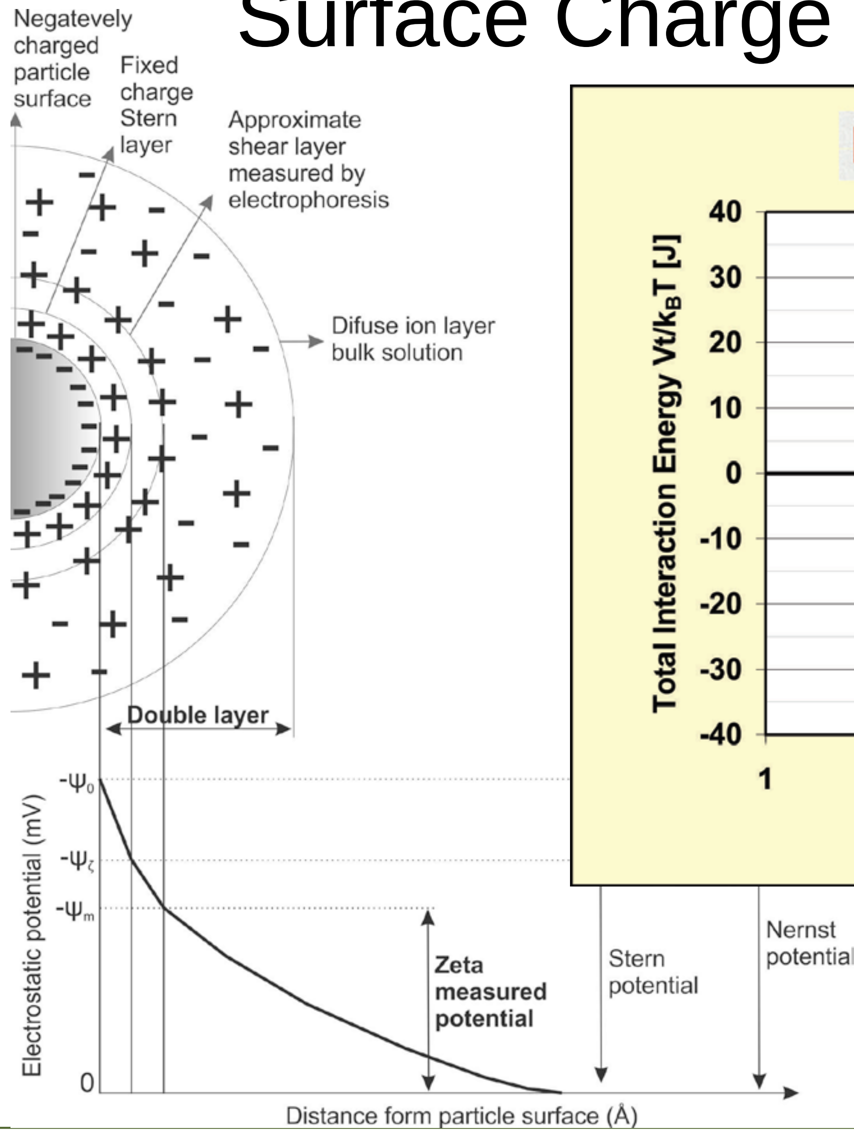
Filter Theory Effects

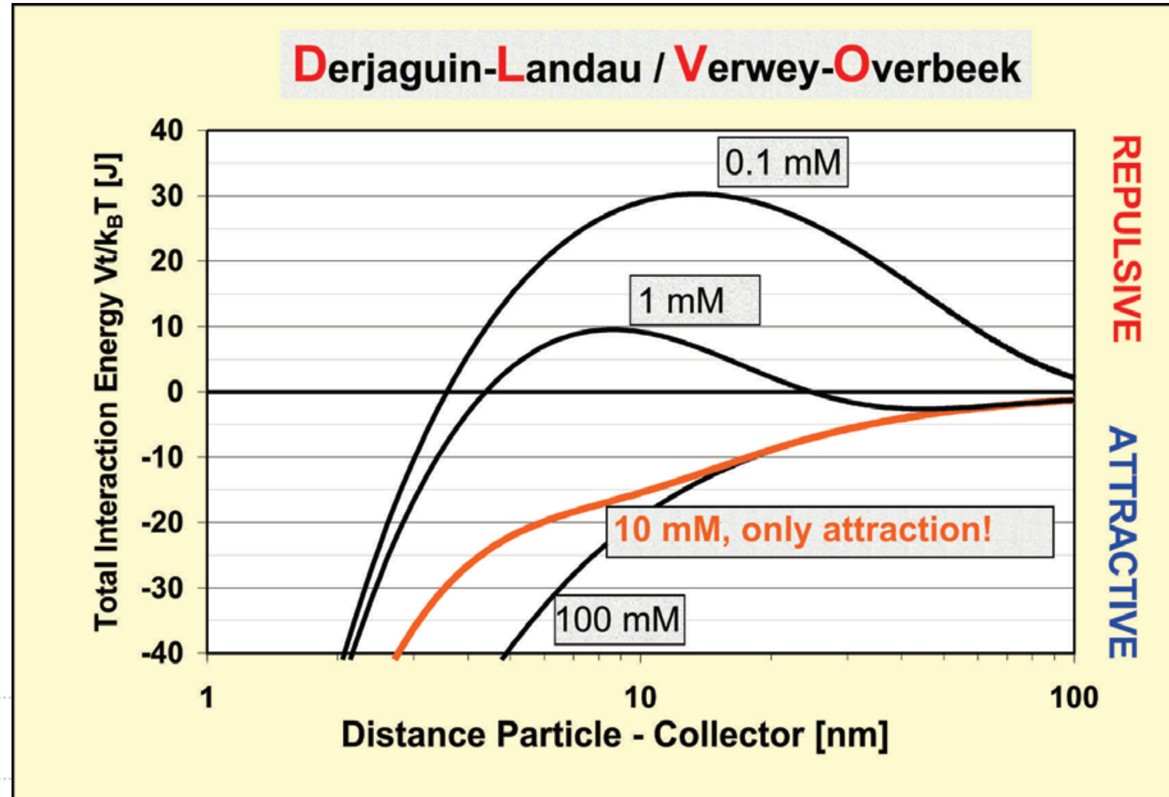
- sedimentation
- interception
- diffusion
- straining

Non- Filter Theory Effects

- gas-water-interface
- film flow
- pH, redox, ionic strength, **heterogeneity**

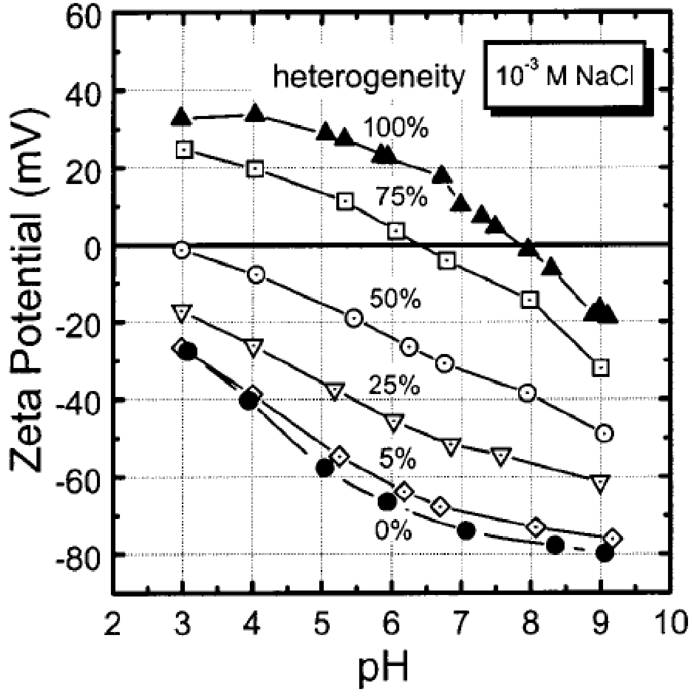
Surface Charge and Ionic Strength



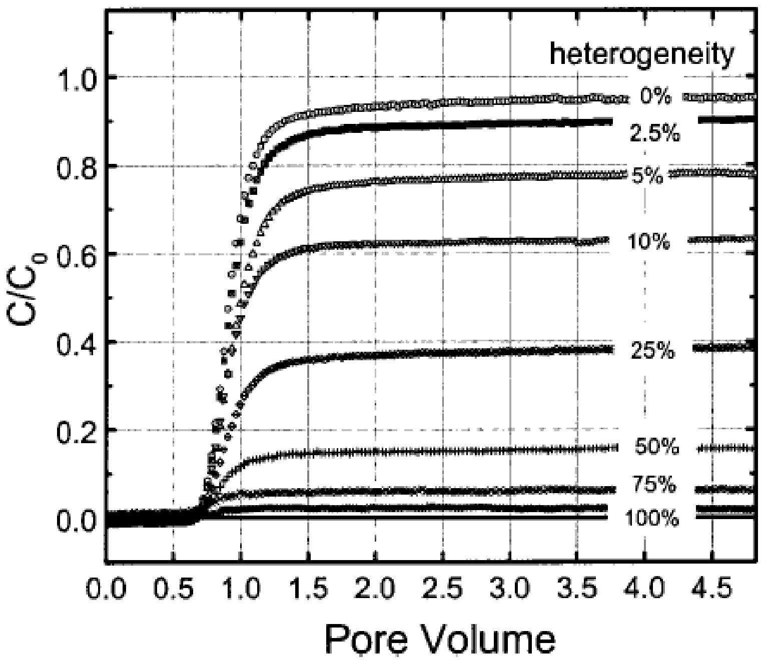


Charge heterogeneity

ζ Potential for clean and heterogeneous sand



Colloid transport in clean and heterogeneous sand



Elimelech et al, 2000, EST 34 (11)

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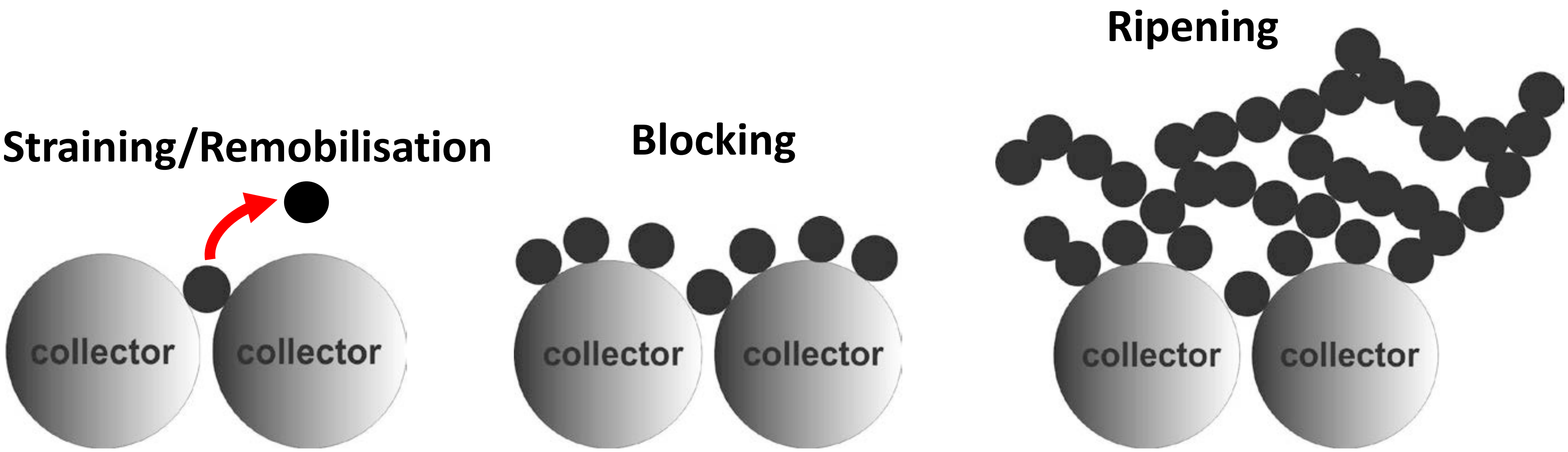
Remobilisation, Ripening, Blocking



Take home message so far…

✓ Injection techniques are important (not WP4)

✓ You need to stabilise your particles
- more charge (coating, works good)
- steric stabilisation (polymers, works good)
- change viscosity (additives, works good)

and/or

✓ You need to work on your aquifer
- less ionic strength (in general not feasible)
- block charge heterogeneities by pre-injection (add costs)

WP 4 Workpackage: 9 Partners

WP 4 used seven different Nanoparticles

- Nanofer 25S (NANO IRON s.r.o., Spolchemie I)
- Nanofer STAR (NANO IRON s.r.o., Spolchemie I)
- Milled ZVI - FerMEG12 (UVR-FIA GmbH, Solvay)
- Carbo-Iron® (ScIDre GmbH, UFZ Leipzig, Balassagyarmat)
- Nano-Goethite (University Duisburg-Essen, Spolchemie II)
- Trap-Ox Fe-zeolites (UFZ Leipzig, premarket phase)
- Bionanomagnetite (University of Manchester, Lab to premarket phase)

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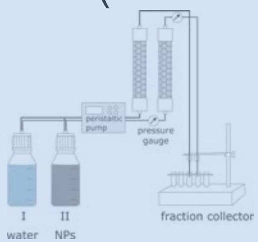
Experimental protocol - deliverable DL.4.1 and Milestone M2

Two Column setups

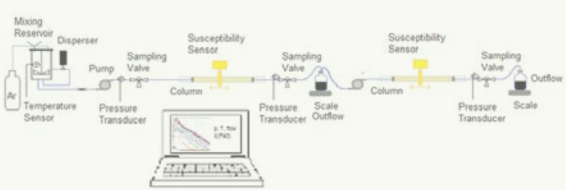
1. Columns (+ modelling)

- D.I (L < 20−30 cm)
- D.II (L > 20−30 cm)



2. Cascading columns

- D.II



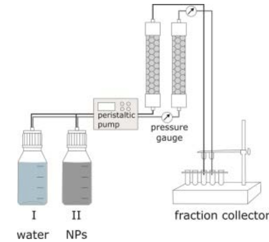
Various Parameters

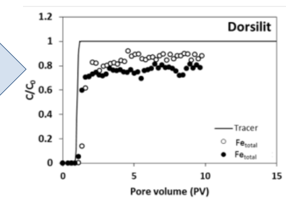
– **Collectors**
  - M.I (DORSILIT® Nr.8)
  - M.II (VEGAS sand)
  - Field site material

– **Solution chemistries**
  - Standard US EPA water with different hardness (F.I.s., F.I.m, F.I.h)
  - Groundwater from field sites

– **Flow conditions**
  - Injection
  - Groundwater flow

1. Column experiments ↔ Modelling



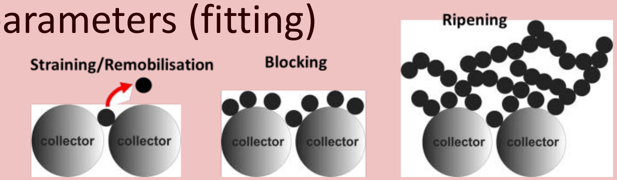


Column tests output

- Breakthrough curves
- Material properties
  - Dimension
  - Grain size, composition, ζ
  - Porosity
  - Dispersion coeff.
- NP properties
  - Composition
  - Size
  - ζ potential
- Fluid properties
  - Solute concentration
  - Viscosity
- Injection protocol
  - NP concentration
  - Injection rate
  - Duration

MNMs 1D model ***homogeneous site***

- **Inverse mode:** Quantitative analysis on the key transport mechanisms, determining transport parameters (fitting)

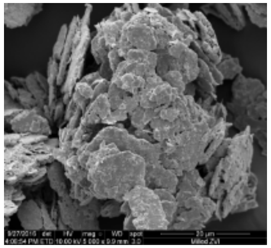


- **Forward mode:** Assuming that transport mechanisms and transport parameters are known, simulation of NP transport under a set of conditions (limits # of column experiments)

MNM3D model ***Remediation design and heterogeneous sites***

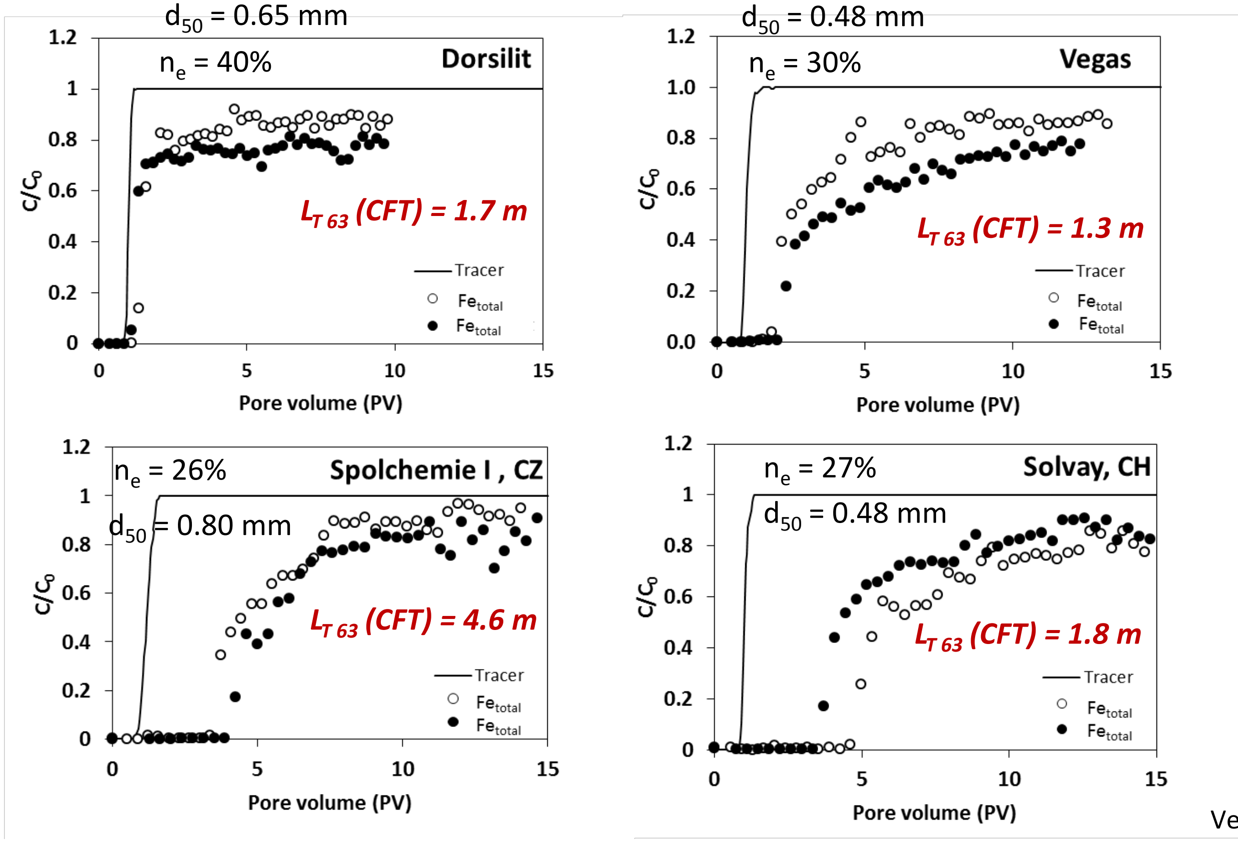
- simulation of particle injection
- prediction of NP fate and transport at the field

Milled ZVI
(FerMEG12, UVR-FIA GmbH)



Source: UNIVIE

***1 g/L agar agar** increased suspension viscosity, ζ potential of milled ZVI (-33 mV) without altering the average particle size (d_{50} = 12 µm)*



- **Unmodified milled ZVI suspensions immobile**
- **Viscous agar agar-stabilized milled ZVI suspension showed good mobility in all porous media**
- Good correlation (R^2 0.90) between the d_{50} of collector and the max particle removal $L_{T\,99.9}$

Column: 2.5 x 22 cm; $v_{inj.}$ = 100 m/d, solution chemistry: F.I.s; pH 8.5; $c_{0,\,particle}$ = 1 g/L

Velimirovic et al., 2016; STOTEN 563-564, p. 713-723

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Carbo-Iron®
(ScIDre GmbH, UFZ Leipzig)

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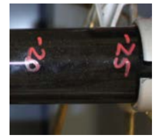
HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

The most mobile suspension contains ***Carbo-Iron®-to-CMC ratio*** *of* ***5***



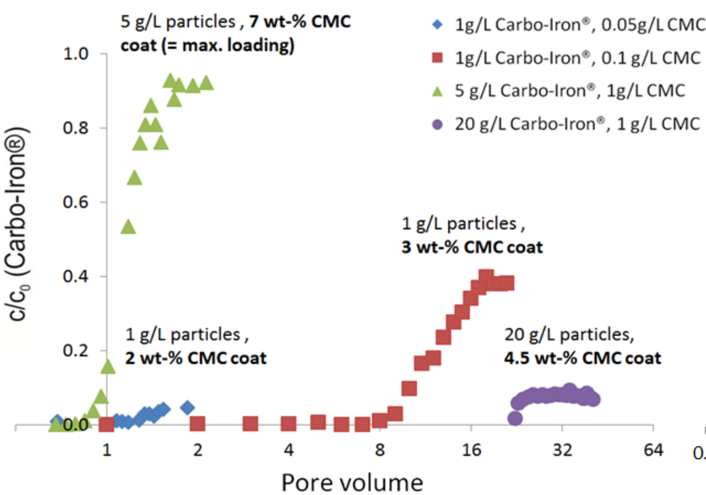
Homogeneous distribution of Carbo-Iron® *in VEGAS sand*

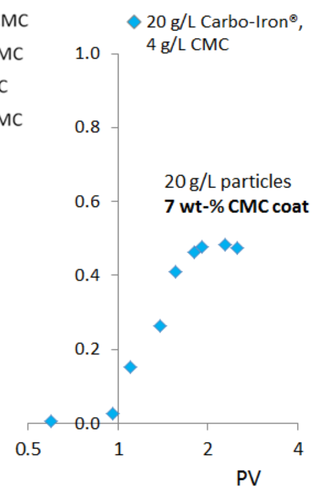
Inhomogeneous distribution of Carbo-Iron® *Balassagyarmat field site, HU*

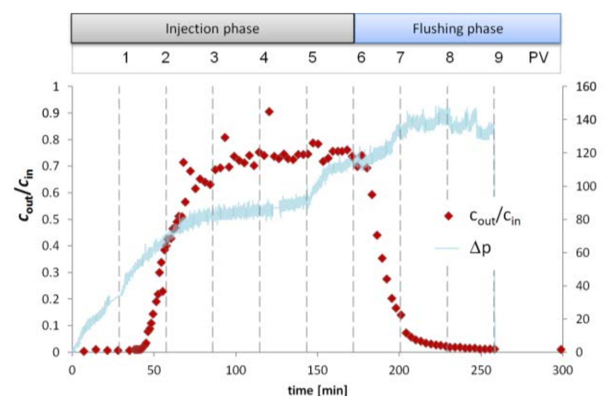
25 cm column, Dorsilit sand

1 m column, VEGAS sand

$L_{T\,63}$ (CFT) = ca. 0.7 m







Collector: Dorsilit® Nr. 8 sand; n_e = 0.37; Column: 1.6 x 25 cm; v_{eff} = ca. 10 m/d; solution chemistry: F.l.m.

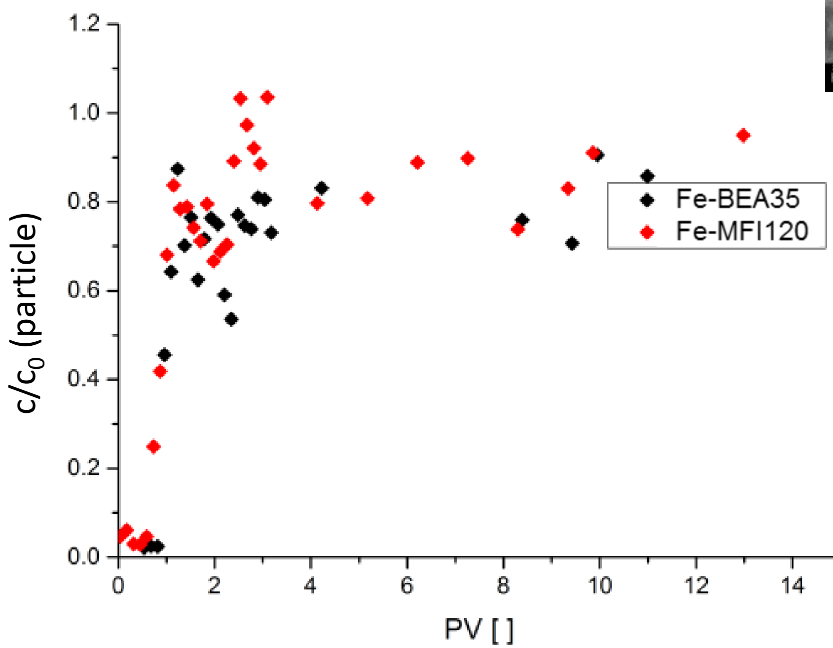
Collector: VEGAS sand; n_e = 0.37; Column: 3 x 100 cm; v_{eff} = ca. 10 m/d; water: F.l.m.

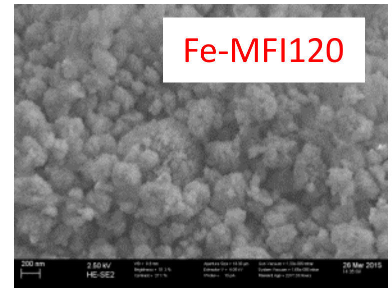
Collector: PM from Balassagyarmat field site, HU (< 2 mm); n_e = 0.26; Column: 3.5 x 18.9 cm; v_{eff} = ca. 10 m/d; $c_{0\,(Fetot)}$ = 15 g/L; $_{CMC}$ = 1.5 g/L; artificial groundwater; Filtered CMC

Trap-Ox Fe-zeolites
(UFZ Leipzig)

In F.I.h:
d_{50} = 550 nm
ζ = -30.0 mV
pH 8.5

High mobility of Trap-Ox Fe-zeolite suspensions without stabilizers





In F.I.h:
d_{50} = 840 nm
ζ = -27.7 mV
pH 8.5

$L_{T\,63}$ (CFT) = ca. 1 m

Collector: Dorsilit® Nr. 8 sand; n_e = 0.38; Column: 1.7 x 20 cm; $v_{inj.}$ = 10 m/d, solution chemistry: F.I.h; pH 8.5; c_0 = 10 g/L)

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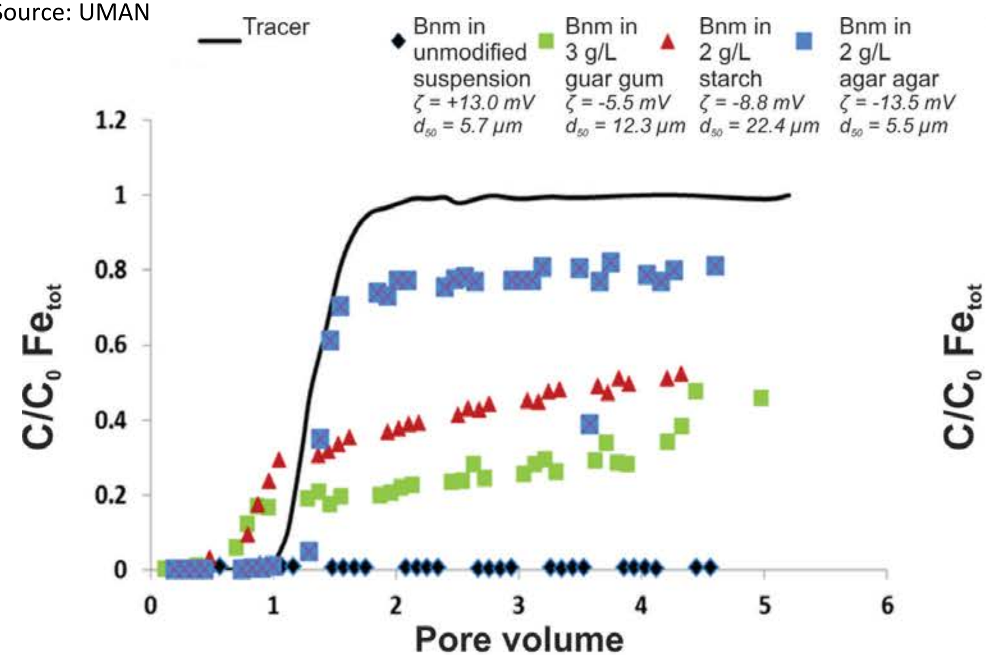
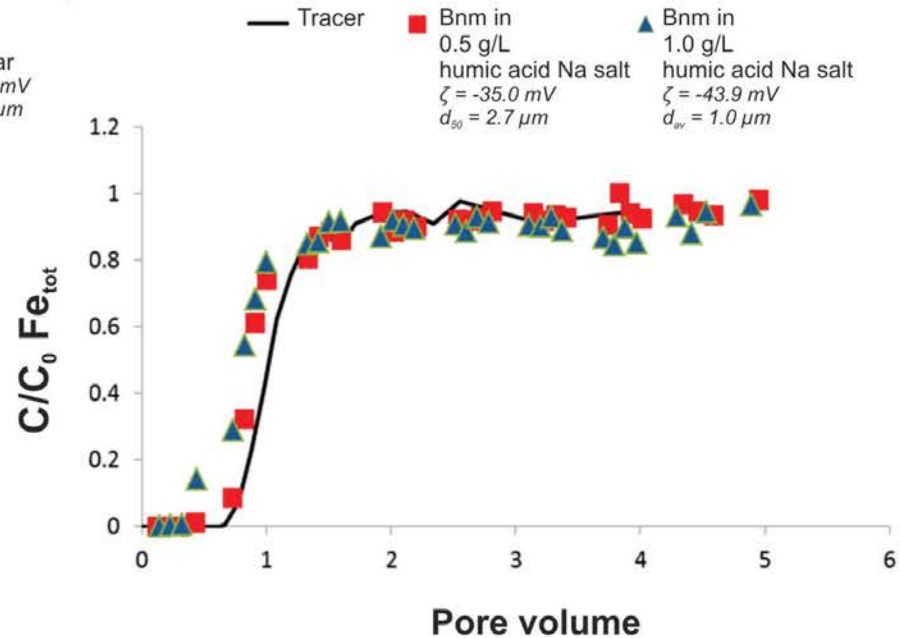
Bionanomagnetite (Bnm) (University of Manchester)

Source: UMAN

Humic acid Na salt as stabilizer provides the highest mobility of Bnm suspension



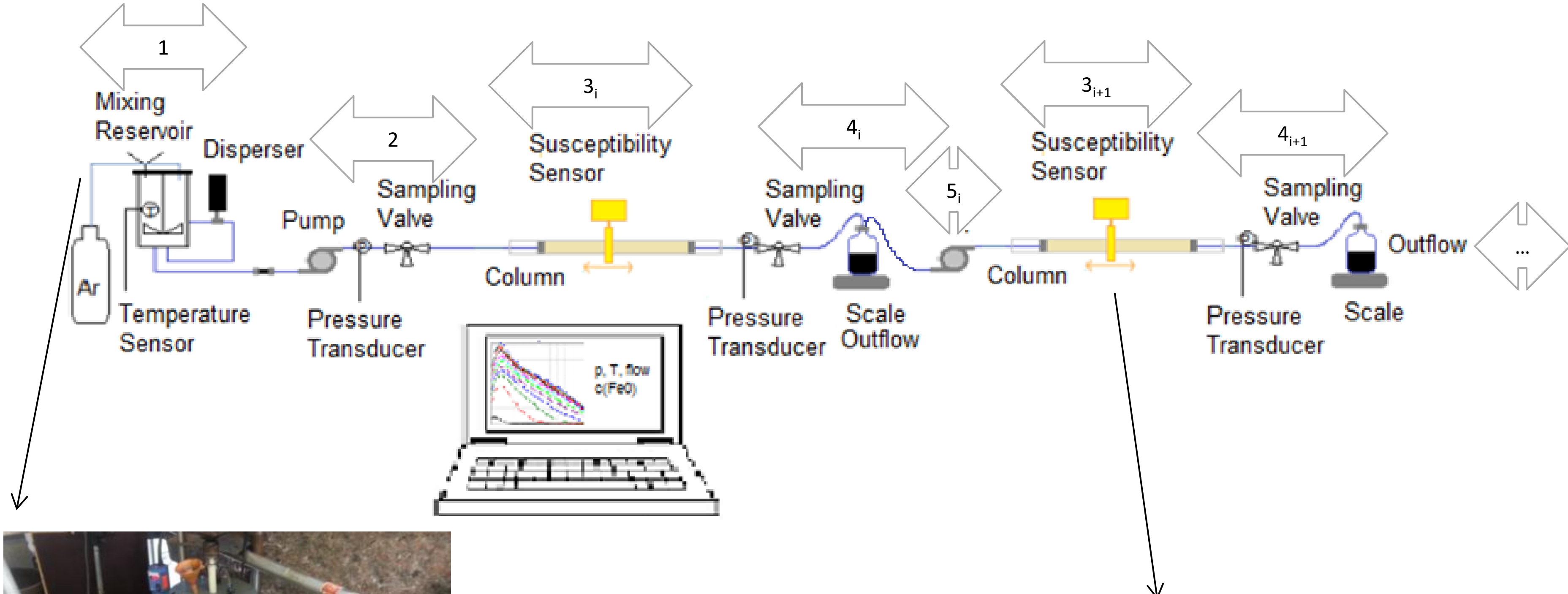
$L_{T\,63}$ (CFT) = ca. 0.5 m



$L_{T\,63}$ (CFT) > 2 m

Collector: Dorsilit® Nr. 8 sand; n_e = 0.37; Column: 2.8 x 11.5 cm; $v_{inj.}$ = ca. 100 m/d; $c_{0\,(Fetot)}$ = 1 g/L; solution chemistry: F.I.s.

2. Cascading column experiments



NANOFER 25S
(NANO IRON s.r.o.)

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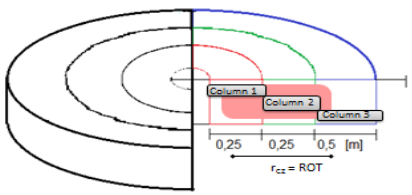
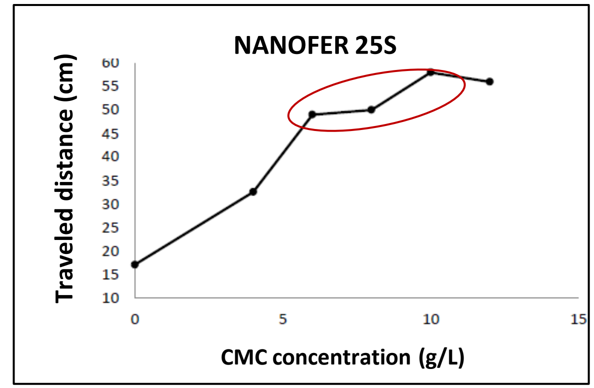
VEGAS

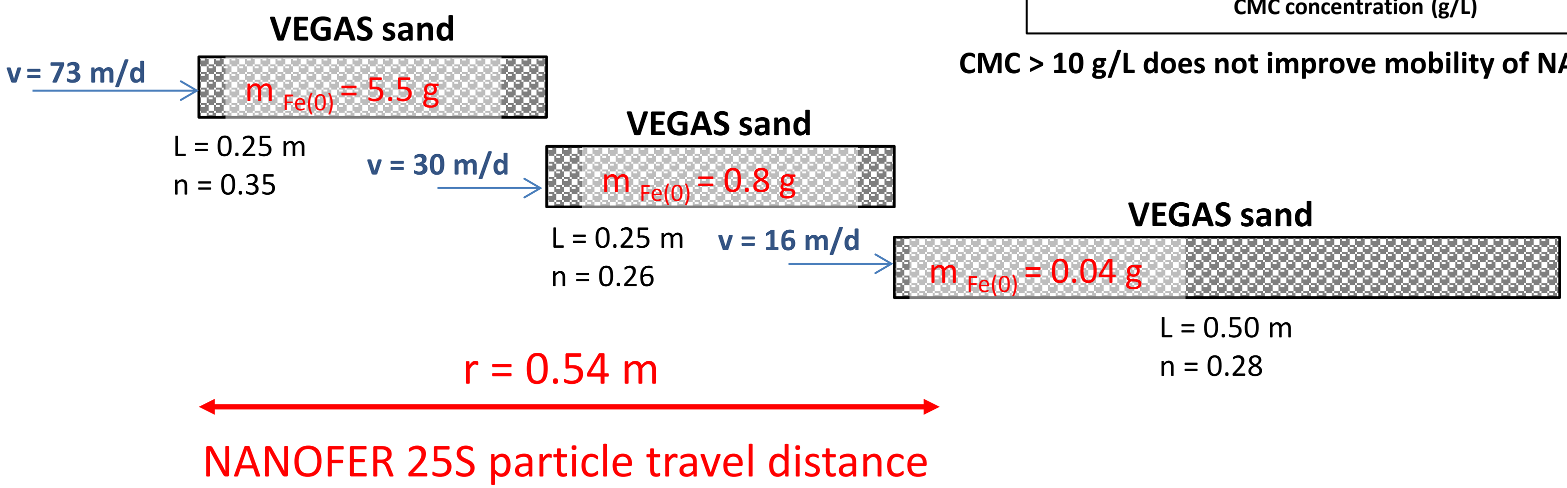
Versuchseinrichtung zur Grundwasser- und Altlastensanierung

Optimal particle delivery to 0.5–0.6 m in VEGAS sand was achieved with CMC-modified suspensions containing 10 g/L Fe(0) and ***stabiliser 5–10 g/L CMC***



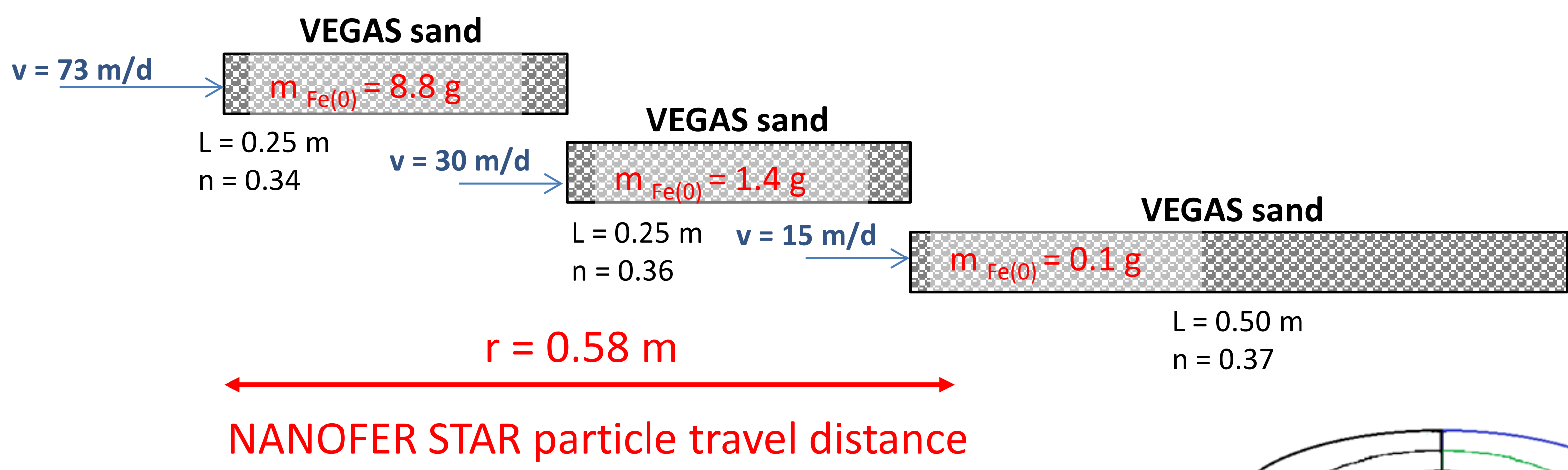


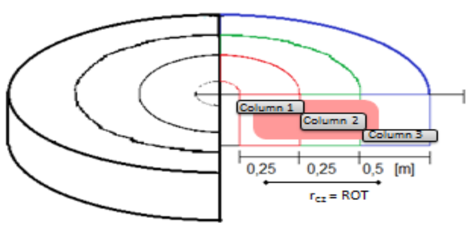
CMC > 10 g/L does not improve mobility of NANOFER 25S



NANOFER STAR
(NANO IRON s.r.o.)

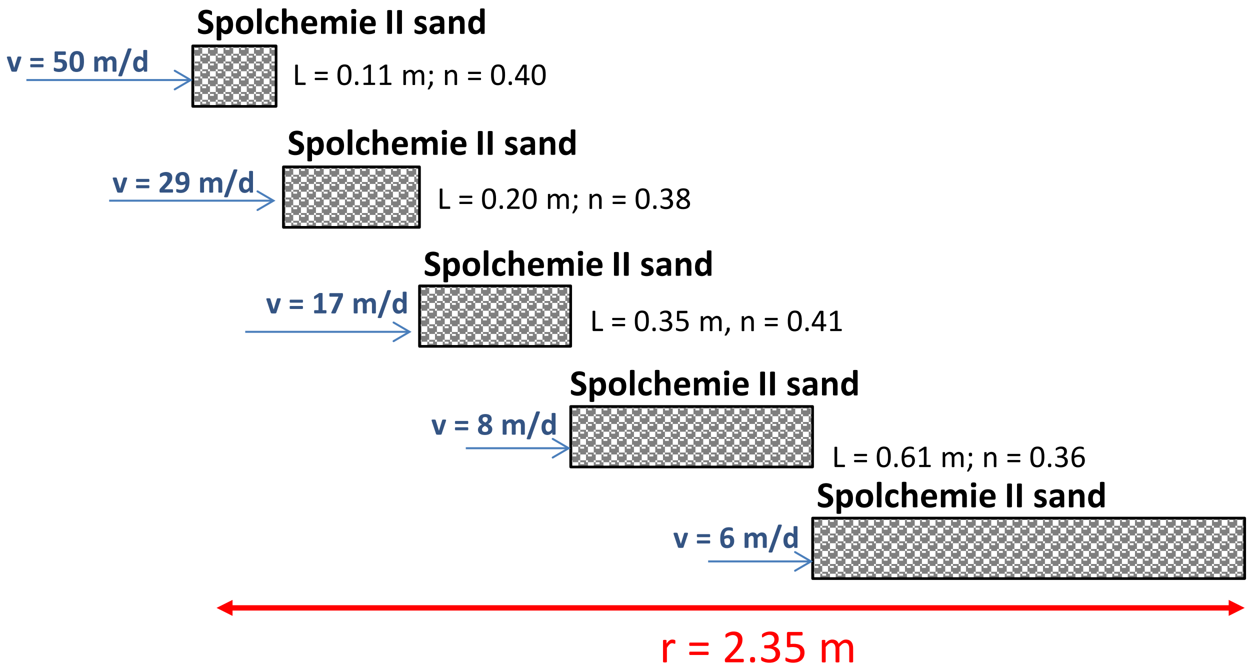
Optimal mobility of NANOFER STAR particles (ca. 0.6 m) in VEGAS sand achieved for the suspension containing $C_{NANOFER\ STAR}$ = 10 g/L and ***stabiliser C_{CMC} = 10 g/L***





Nano-Goethite
(University of Duisburg-Essen)

- ***Particle stabilizer: humic acid;*** *d_{50} = ca. 450 nm; ζ = -56 mV*
- *86% of the initial Fe after 2.35 m, very mobile*
- *75% of particle organic coating lost during the transport → reducing risk for renegade particles*



86% of Nano-Goethite particle traveled beyond this distance

Generalized Guideline Transport

Analyse field site material: grain size, mineralogy, water chemistry

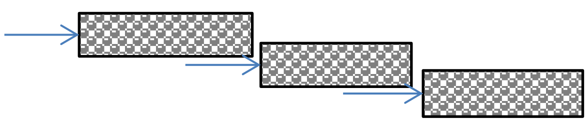
↓

Run column experiments with field material and water or a surrogate (< 5 mm)

Cascading columns | *„Simple“ 1D columns*

Cascading columns

Respect injection scenario (flow velocity)



→ Determine radial NP distribution

→ Determine changes needed for injection

↓↓

Field injection

addapt (back to cascading columns)

„Simple“ 1D columns

See Experimental Protocol DL 4.2 ☺

- Homogenous material ↓ **1D** model
- Heterogenous and remediation design ↓ **3D** model

↓↓

Optimised parameters for field injection, upscaling

Thank you for your attention

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