Non ZVI: Design, Performance and Application Possibilities

Katrin Mackenzie, UFZ

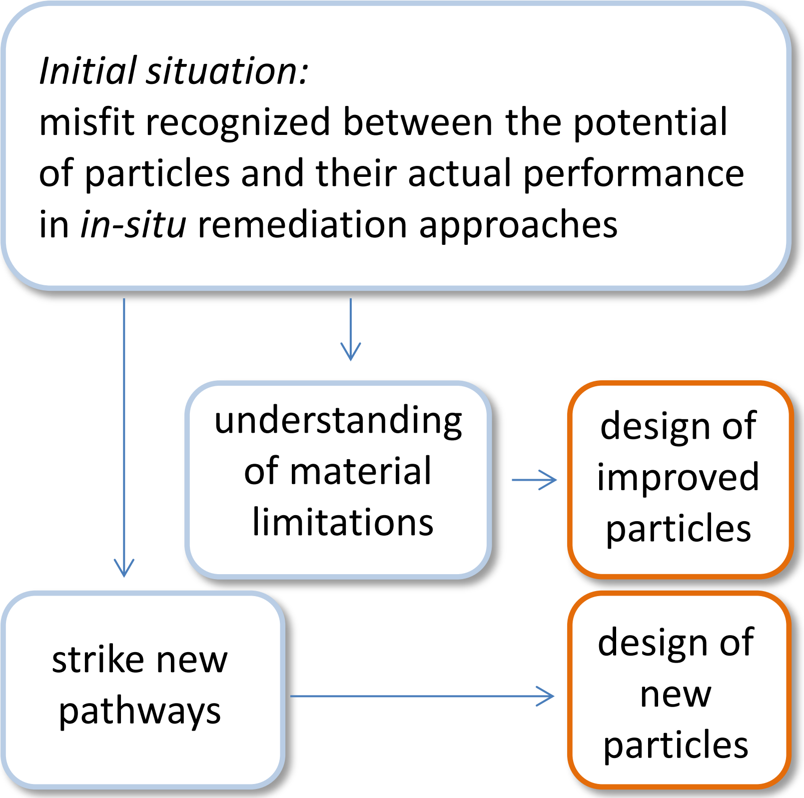
NanoRem Final Conference

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

Frankfurt am Main, 21st November 2016

Why new particles? Project aims.

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment



Initial situation:
misfit recognized between the potential of particles and their actual performance in *in-situ* remediation approaches

understanding of material limitations

design of improved particles

strike new pathways

design of new particles

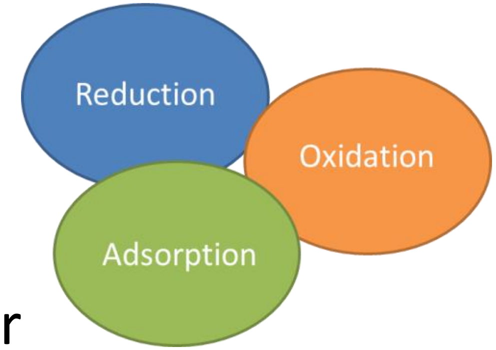
Aims:

→ Environmentally benign products

→ Improved injectability and subsurface mobility

→ Suitable not only for plume, but also source (zone) treatment

Particle types


Reduction

Oxidation

Adsorption

- Overview of non-ZVI particles
- Summary of abilities and limitations for each particle type

Nano-Goethite

Carbo-Iron®

Trap-Ox Fe-Zeolites

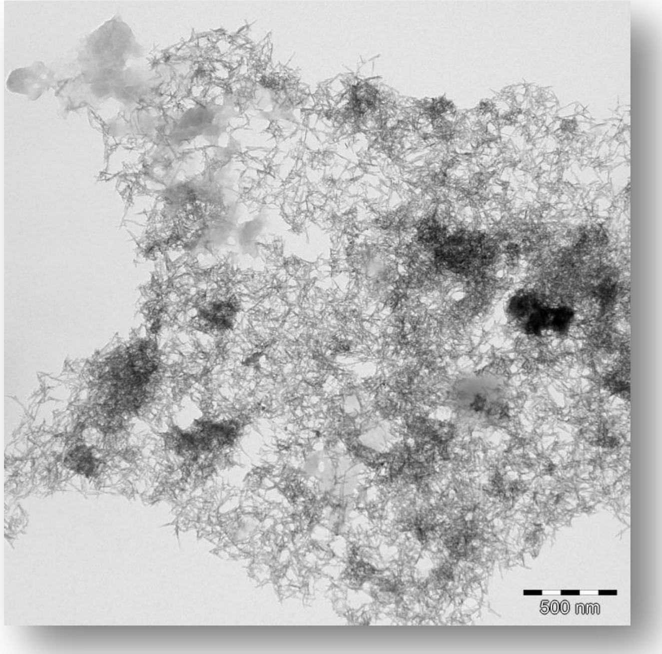
Bionanomagnetite (Pd)

Barium Ferrate

Non-ZVI metals

Nano-Goethite

Goethite: $\alpha\text{-Fe}^{3+}O(OH)$



TEM image of Nano-Goethite particel (aggregates)(© UDE)

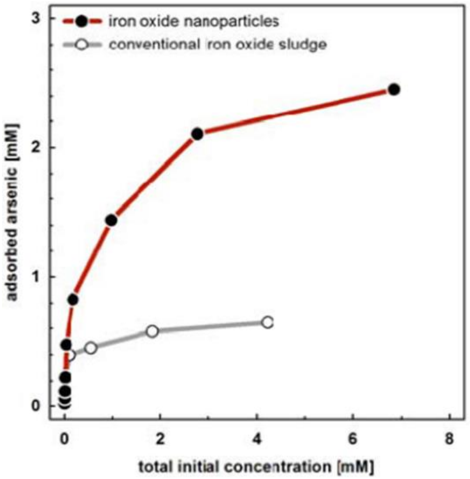
Nano-Goethite are **colloidal, nanosized iron oxide particle**, coated with a layer of natural organic matter polymers.

Two major application strategies where the iron oxides are readily available for

- ✓ **adsorption of heavy metals or as**
- ✓ **electron acceptors for microbial iron reduction.**

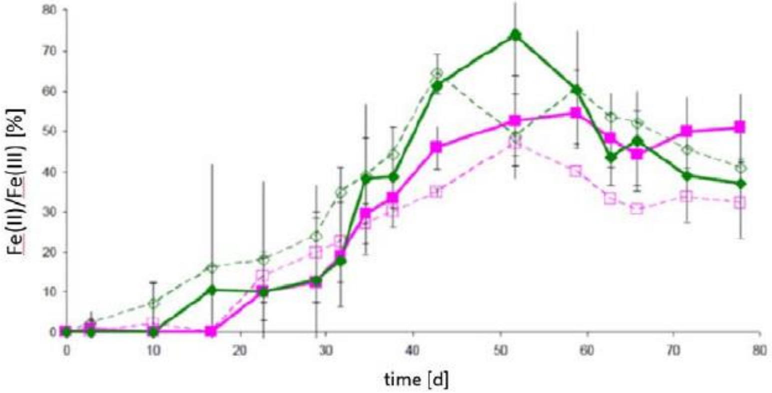
Nano-Goethite

Arsenic adsorption



Batch adsorption isotherm of arsentite at pH = 7 in a low-salt groundwater medium (red: nanosized iron oxide, gray: bulk iron oxide; Sigma goethite, size > 1 µm)

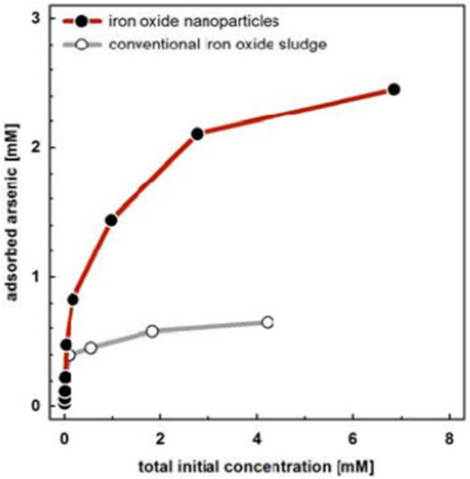
Toluene degradation



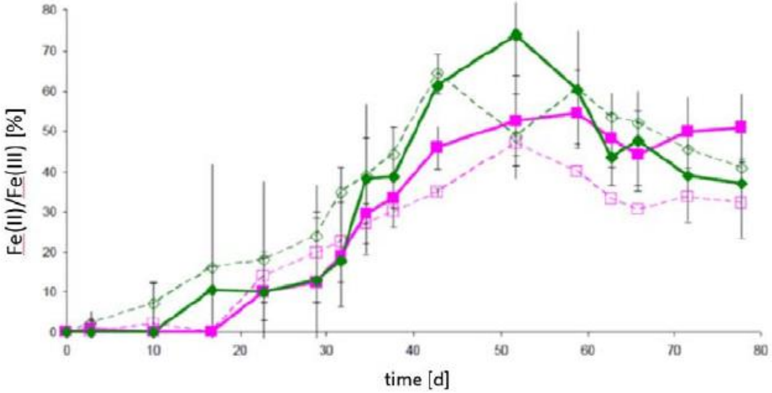
Nano-Goethite amended with BTEX contaminated sediments spiked with toluene (1µM). Green: nano-ferrihydrite. Pink: Nano-Goethite. Open symbols: no coating. Full symbols: humic acid coating. Geobacter sulfurreducens was added as an iron-reducing model microorganism. $c_{Fe\text{-}oxide}$ = 4 mM

Nano-Goethite

Arsenic adsorption



Toluene degradation



- Adsorption of heavy metals at NP surface (e.g. As)
- Greatly enhanced microbial iron-reduction is utilized for contaminant degradation (e.g. BTEX)
- Humic acid coating provides mobility (over several meter) and supports the bioremediation

Nano-Goethite

Injection at VEGAS large-scale container (© VEGAS)

Nano-Goethite injection at SPOLCHEMIE site (© UDE)

Successful up-scaling of iron oxide-related bioremediation

- Large-scale container at VEGAS: 100 days bioremediation observed after injection, 60% Nano-Goethite utilized

- 300 kg Nano-Goethite injected in a pilot area (SPOLCHEMIE II, Usti nad Labem, CZ) contaminated mainly with BETX.

- Marked degradation of toluene

Nano-Goethite


Injection at VEGAS larg


Nano-Goethite injection

LCHEMIE site (© UDE)

Development state:

“Field tested and ready for market“

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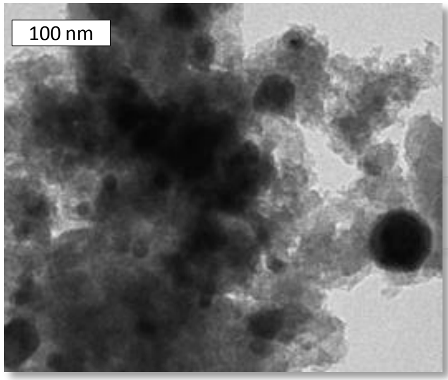
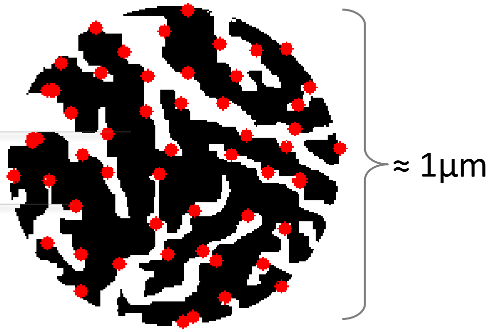
Carbo-Iron®



TEM image of Carbo-Iron® (© UFZ)

Carbon backbone

Fe nanoclusters



(© UFZ)

Carbo-Iron® is an air-stable, **colloidal composite of AC + Fe^0** with 25…30 wt% nanosized iron embedded in <1µm activated carbon

- ✓ Properties from both materials
- ✓ Strong adsorption at carbon and thus enrichment and increased retention of contaminants in the reaction zone
- ✓ Sorption increases efficiency of reduction at Fe^0

Carbo-Iron®

Initial Carbo-Iron injection phase

Remaining particles at organic surfaces
(© UFZ)

- Affinity higher for particle deposition at contaminant phase
- Adjustment of stabilizer concentration (CMC) allows either high mobility (several meters) or injection-near particle placement

Increased suitability for plume and source treatment

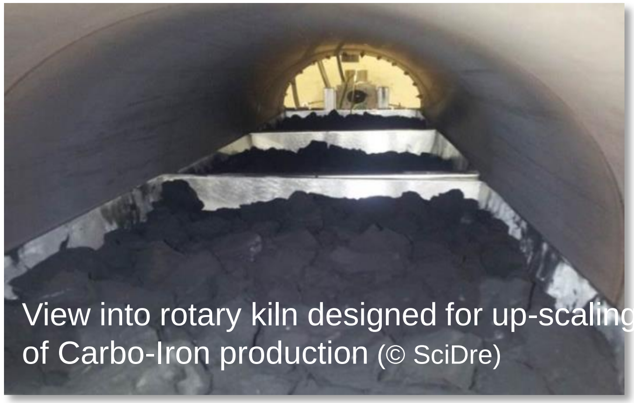
Carbo-Iron®

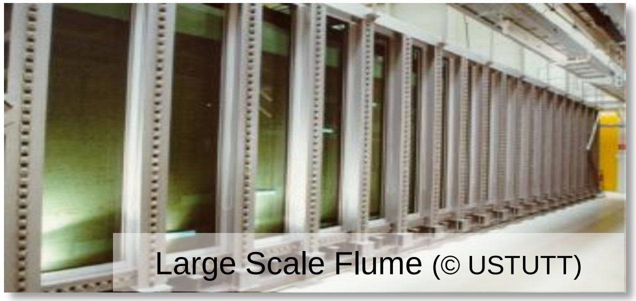
- Transfer from laboratory to **larger scale production:** carbothermal synthesis suitable for production at industrial scale (cooperation UFZ – SciDre)

- **Up-scaled testing:** Carbo-Iron for Large-Scale Flume (LSF); production for field site injection in Hungary

- **Optimization of suspension recipe:** for targeted particle deposition possible for either plume or source attack

- **Identified application areas:** reduction (proved effectiveness for broad spectrum of chlorinated and brominated hydrocarbons, heavy metals…) support by strong sorption, successive bioremediation phase


View into rotary kiln designed for up-scaling of Carbo-Iron production (© SciDre)


Large Scale Flume (© USTUTT)


Carbo-Iron injection (© UFZ)

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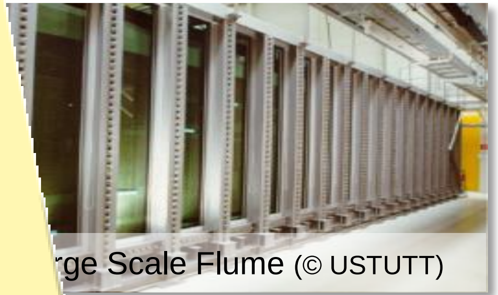
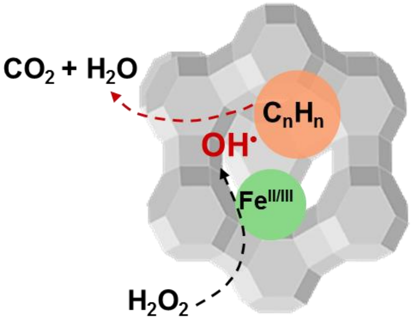

rge Scale Flume (© USTUTT)

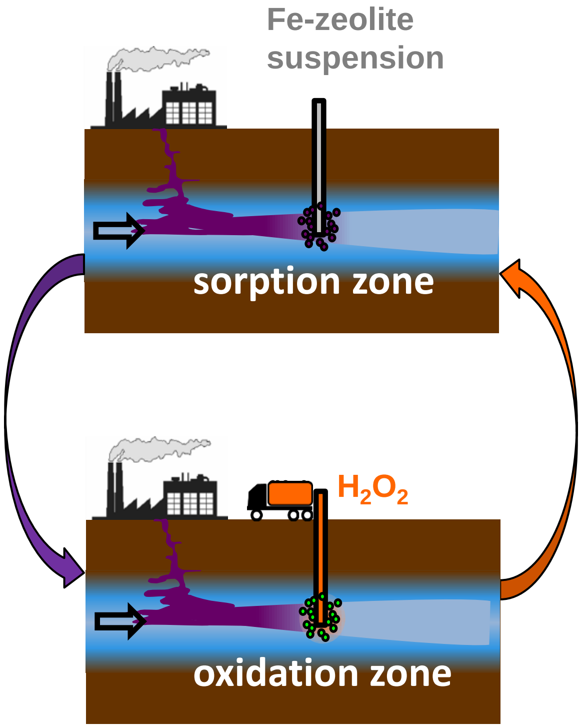

Carbo-Iron injection (© UFZ)

Trap-Ox Fe-Zeolites

Fe-doped zeolites used as sorption-active catalysts to form an *in-situ* **adsorption/oxidation barrier**

- **Extention of nanoremediation application range** towards contaminants not amenable to reduction (by NZVI) and/or biodegradation



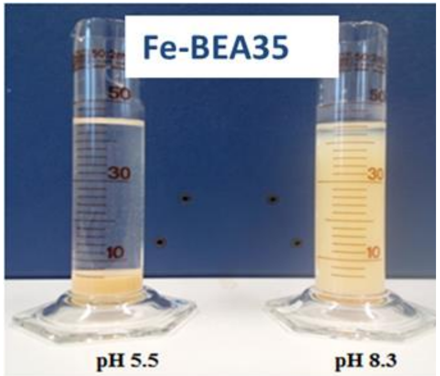


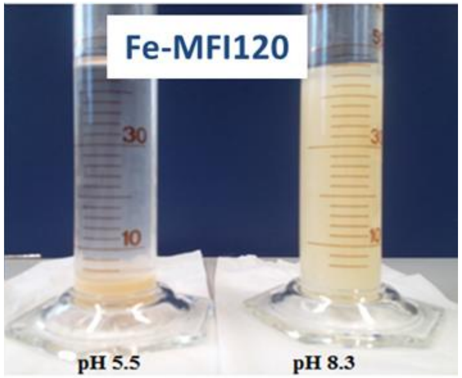
- Trap contaminants from migrating plumes or matrix-back diffusion → targeted oxidant application
- Catalyst and H_2O_2 injected separately → less safety problems
- Reaction at neutral pH → no additional additives

advantage over conventional ISCO

Trap-Ox Fe-Zeolites

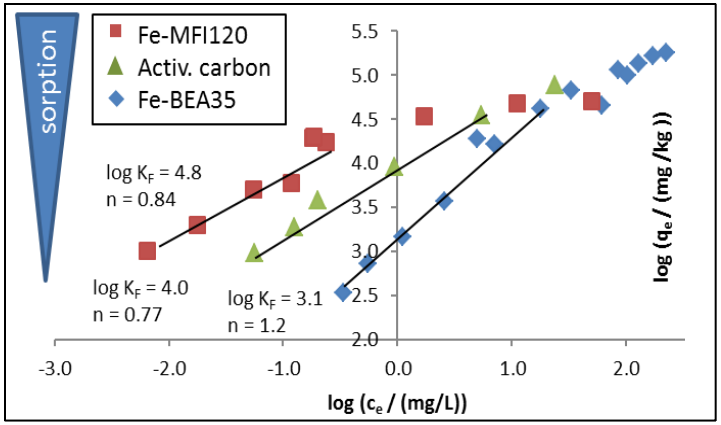
Stable suspensions (24 h, 10 g/L Fe-zeolite) without stabilizer

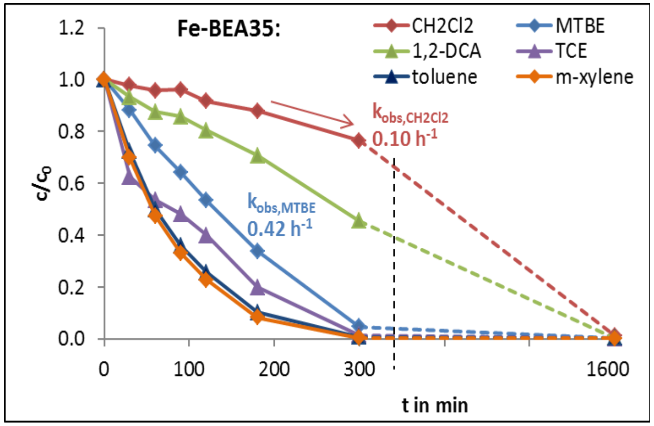




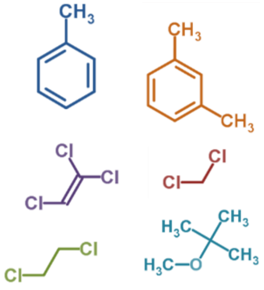
(© UFZ)

Excellent adsorption of MTBE and degradation of various contaminants



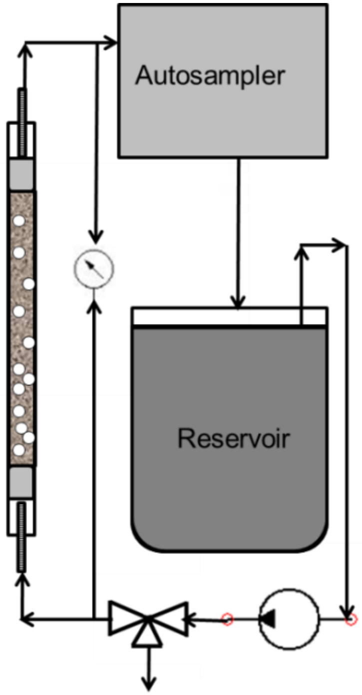


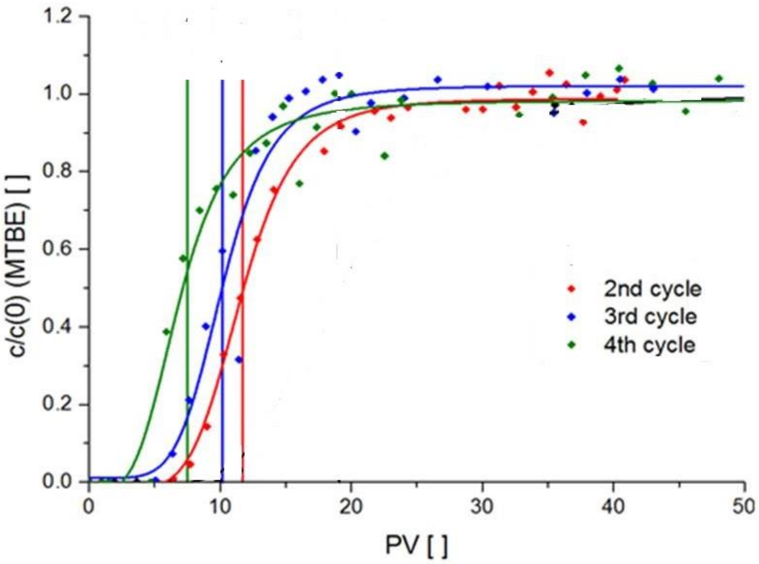
$c_{Fe\text{-}zeolite}$ = 10 g/L, $c_{0,contaminant}$= 20 mg/L,
$c_{0,H2O2}$ = 8 g/L, medium: F.I.s, pH = 7



… and other contaminants: surfactants, pharmaceuticals, …

Trap-Ox Fe-Zeolites

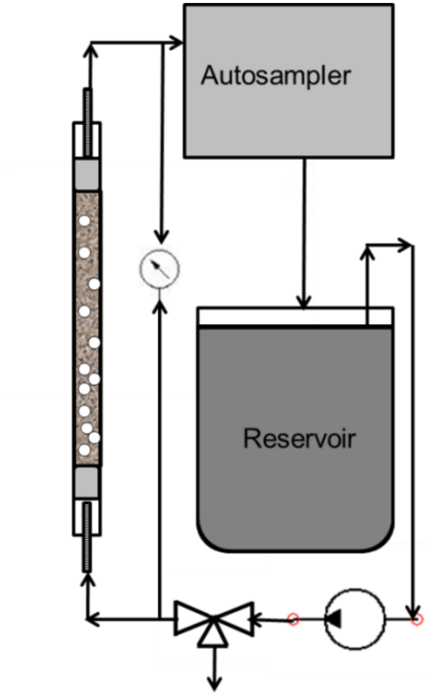


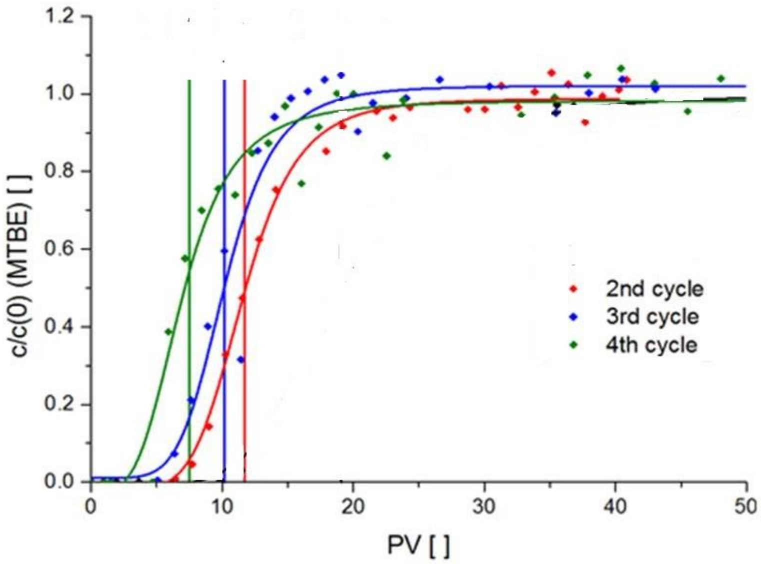


Several sorption/regeneration cycles : breakthrough of MTBE in 20 cm column loaded with 0.2 wt% of Fe-BEA35

- Trap-Ox Fe-BEA35 active for adsorption and catalytic oxidation even beyond 4 adsorption/regeneration cycles (2 months)
- Aging in very hard water containing NOM (38 days) altered content of divalent cations, but Fe^{3+} content and BET area nearly unchanged

Trap-Ox Fe-Zeolites





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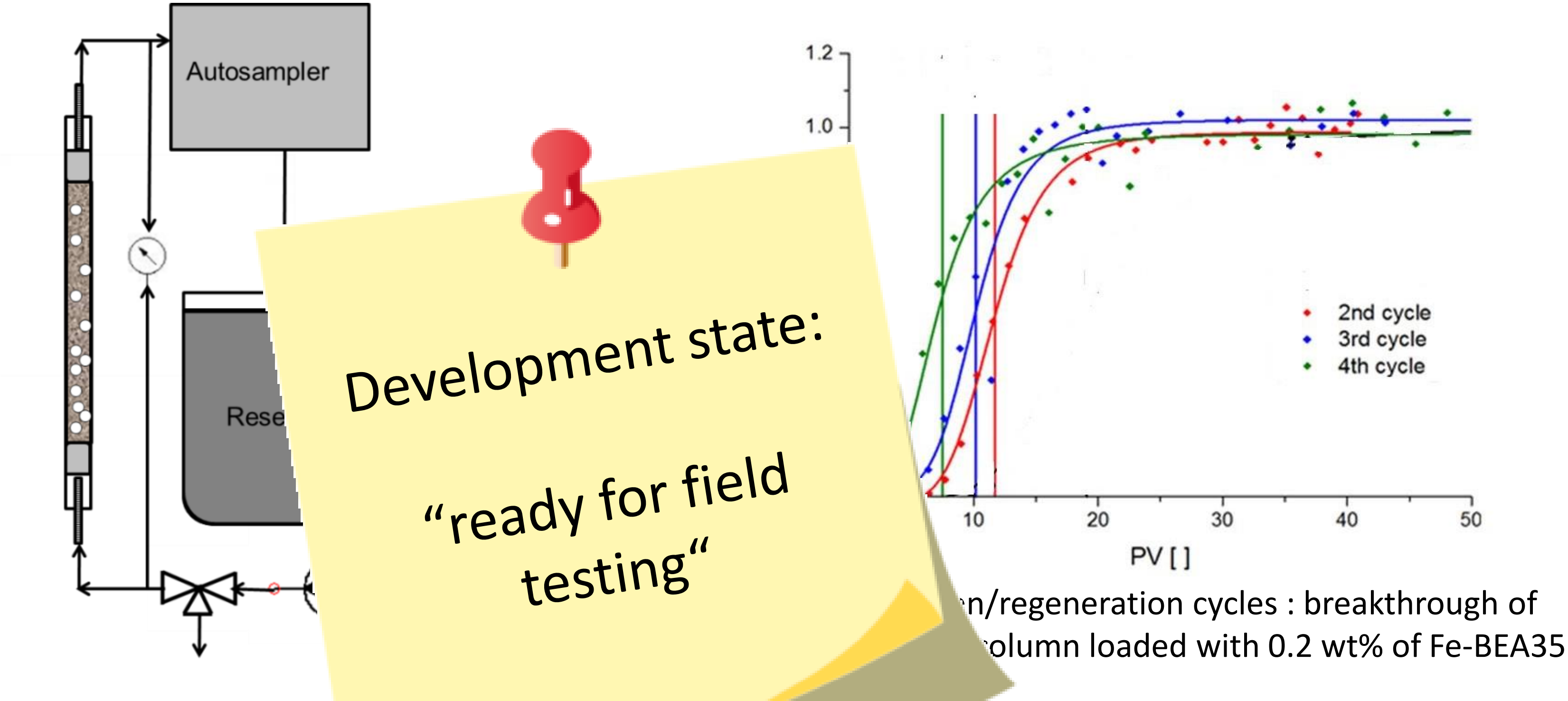

Development state:

“ready for field testing“

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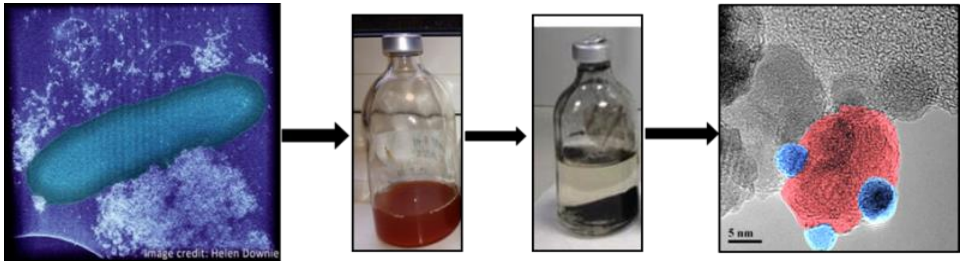
Bionanomagnetite (Bnm)



Bacteria added to ferrihydrite to form Bnm

Doping with Pd

(© UMAN)

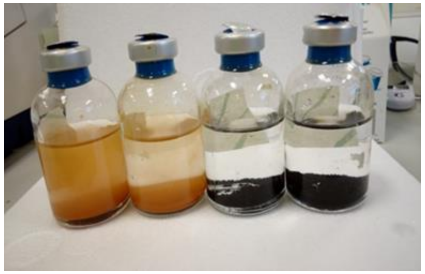
Fe(III)-oxide/hydroxide

↓ *Geobacter sufurreducens*

Fe(II)(III) oxide

The bioproduced nano-sized Fe_3O_4 can be

- synthesized in higher amounts – scalability for field application in future
- and from alternative sources, such as natural Fe-based sediments



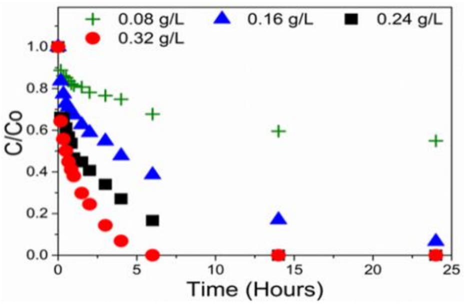
Natural Fe-based sediment as precursor
(© UMAN)

Bnm is able to effectively

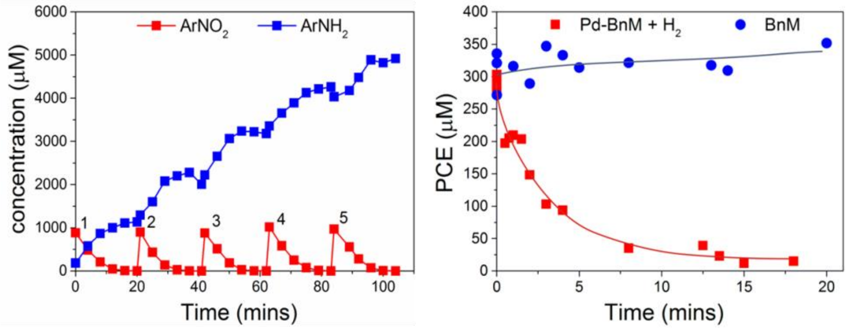
- **adsorb** metal ions,
- provides **reduction** equivalents
- With modification of the surface using green stabilizers (e.g. humic acid, guar gum), Bnm shows enhanced mobility.

Bionanomagnetite (Bnm)

- **Adding Pd** as catalyst results in extended treatable contaminant spectrum.
- Potential applications of Bnm and Pd-Bnm in remediating metals (Cr(VI) → Cr(III) used as example) and organic solvents (PCE and nitrobenzene used as examples).
- Field-near laboratory experiments: Sediments from Spain were tested and Bnm has shown to immobilize chromite ore processing residues from a mine in Glasgow.



Cr(VI) removal with increasing additions of Pd-Bnm as example for metal adsorption



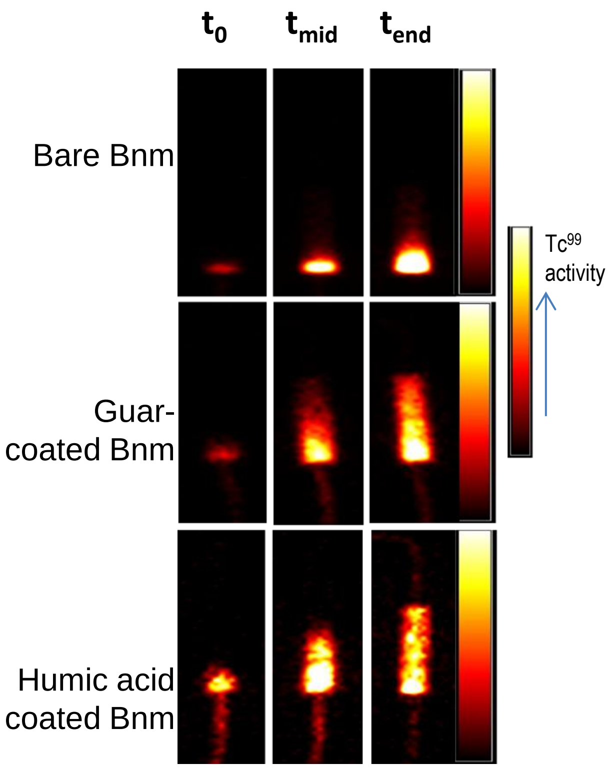
Reduction of amine contaminants (e.g. ArNO$_2$, left) chlorinaded ethene (e.g. PCE, right) in the presence of Pd-BnM/H$_2$

Bionanomagnetite

Working with **radiotracers** (e.g. Tc^{99}) provided results on

- The reductive adsorption of the Tc on Bnm following Tc(VII) → Tc(IV) used to label the Bnm
- Mobility of the labelled Bnm in column experiments

Transport experiments with Bnm utilized the instantaneous attachment of the metastable isomer Tc^{99m} for gamma imaging. Removal of radionuclides is one of the promising application areas of Bnm.



Colloid stabilizer effect on the transport of Tc-marked Bnm through sediment-filled column

(© UMAN)

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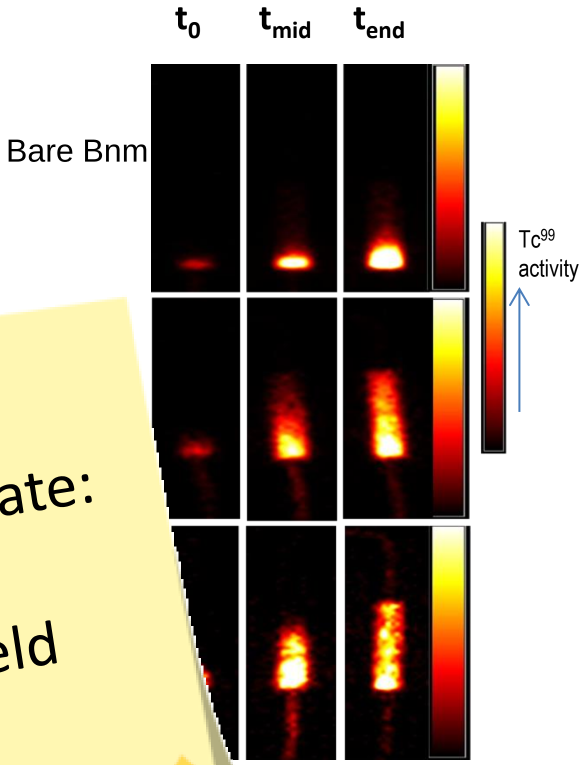


tabilizer effect on the
of Tc-marked Bnm
ediment-filled column
(© UMAN)

Barium Ferrate

Barium ferrate synthesized at laboratory scale (© VEGAS)

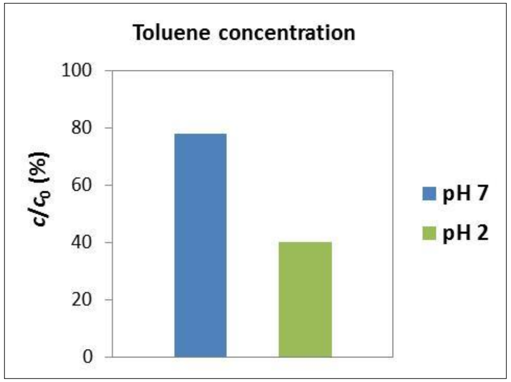
$BaFeO_4$: (Fe^{6+}) as slow-releasing strong oxidant.

- Electrochemical synthesis route most promising with regard to Fe(VI) content
- Chemical oxidation of BTEX contaminants (toluene) tested.

$$FeO_4^{2-} + 8\ H^+ + 3\ e^- \rightarrow Fe^{3+} + 4\ H_2O \qquad E^0 = 2.20\ V$$

$$FeO_4^{2-} + 4\ H_2O + 3\ e^- \rightarrow Fe(OH)_3 + 5\ OH^- \qquad E^0 = 0.72\ V$$

- Toluene degradation is favoured under strong acidic conditions → Limited pratical relevance!
- Formation of intermediates (benzoic acid)
- Pollutant degradation limited by the low conc. of FeO_4^{2-} resulting from the low solubility of $BaFeO_4$



Toluene degradation using $BaFeO_4$ (reaction time 2 weeks, c_0 = 54 mg/L, $n_{\text{ferrate(VI)}}/n_{\text{toluene}} \approx 1.5/1$)

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- Toluene degradation is favoured under strong conditions → Limited pratical relevance!
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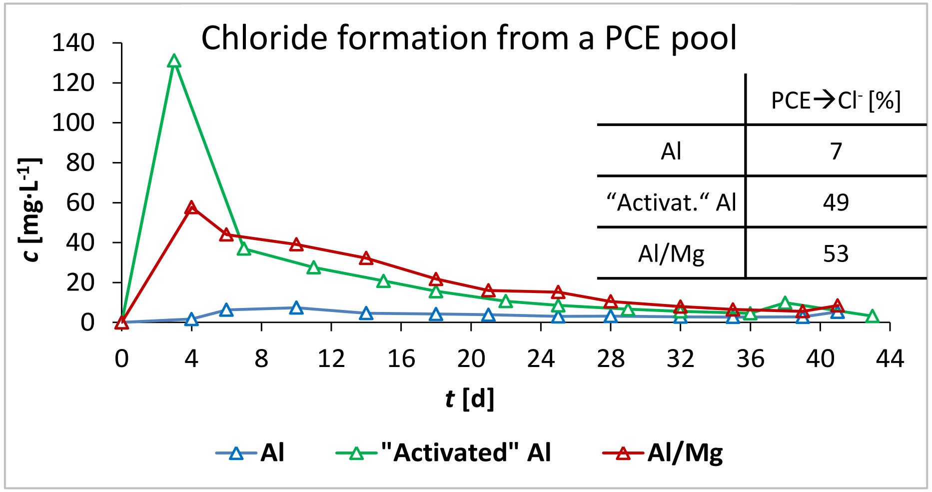
Development state:

“laboratory test“

ing BaFeO$_4$
ime 2 weeks, c_0 = 54 mg/L,
$n_{\text{ferrate(VI)}}/n_{\text{toluene}} \approx 1.5/1$)

Non-ZVI metals: Al and Mg

Studied as possible alternative reactive metal particles to NZVI which have a much lower density and are non-magnetic and thus should offer better mobility than NZVI.



	$PCE \rightarrow Cl^-$ [%]
Al	7
“Activat.“ Al	49
Al/Mg	53

Column experiments under flow-through conditions:

Compared to pure Al and Mg PCE degradation was improved by using

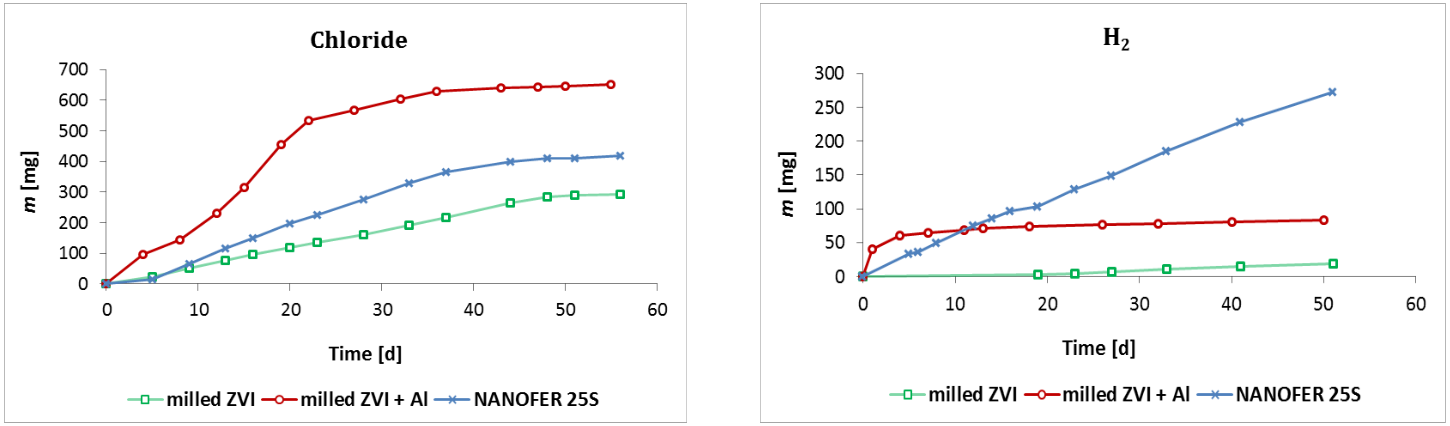
- mechanically activated Al particles, Al/Mg metal alloy particles
- only traces of TCE and DCE and no VC are formed

- Drawback: poor long-term reaction behaviour
- Non-ZVI metals are therefore not recommended for field application.

Iron alloys

Material mixes of Fe/Al, Fe/Mg and Fe/Si were tested - promising results for **Fe/Al** with regard to

- ✓ PCE degradation
- ✓ Dechlorination vs. anaerobic corrosion



Comparison of chloride formation from PCE and corrosion for the three particles under the same conditions

→ Petty patent has been registered.

→ Milling tests (UVR-FIA GmbH) and further reactivity tests are in progress.

Iron alloys

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Comparison of chloride formation i … les under the same conditions

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Achievements?

Reduction

Carbo-Iron®
Bionanomagnetite (BnM)
Palladized BnM
Non-ZVI metals (Mg/Al)

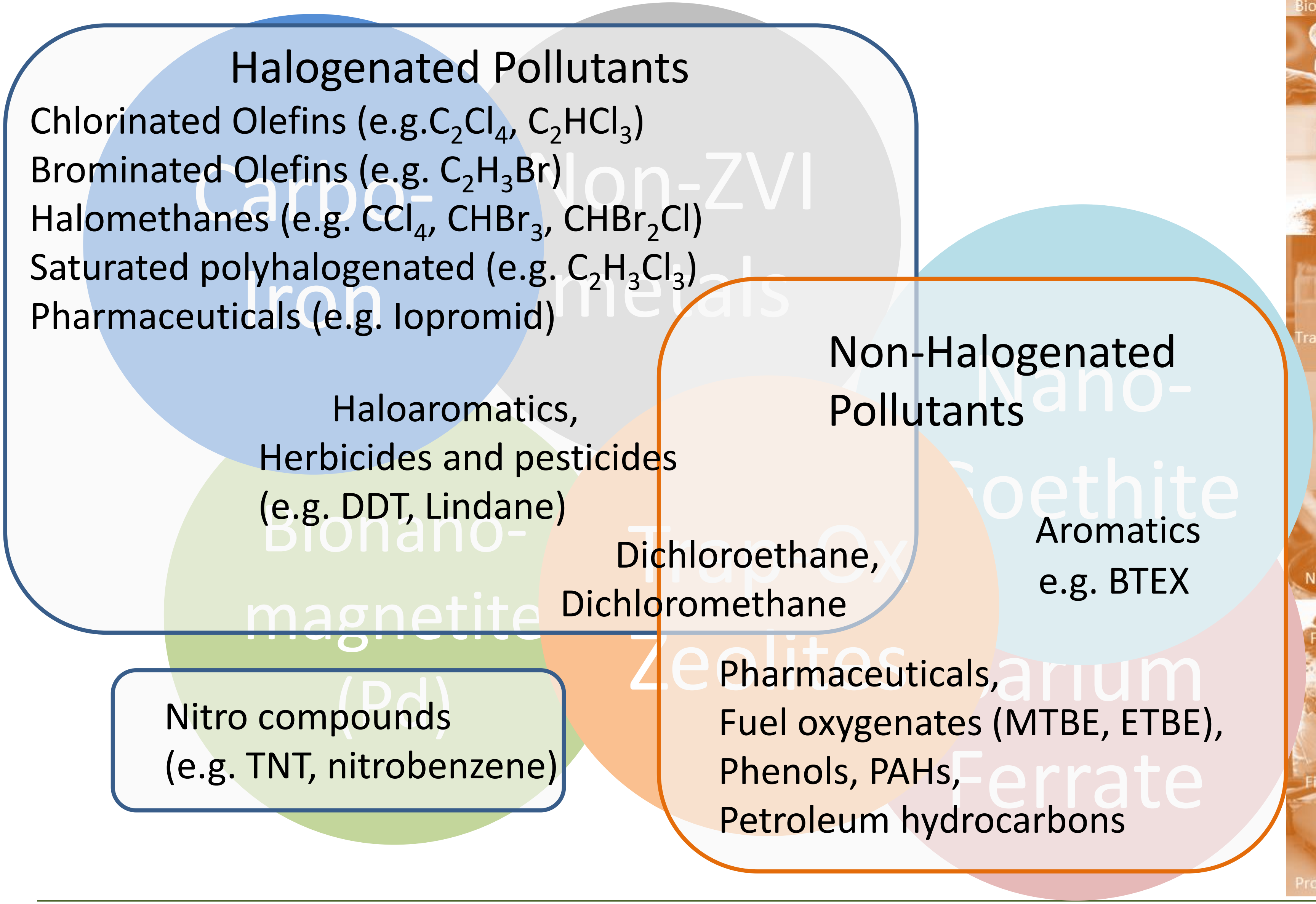
Oxidation

Nano-Goethite
Trap-Ox Fe Zeolites
Barium Ferrate

Adsorption

Nano-Goethite
BnM and Pd/BnM
Trap-Ox Fe-Zeolite®
Aged Carbo-Iron

- → Extended reaction spectrum
- → Target-specific particle design
- → Various development stages
- → 3+ patents



Halogenated Pollutants

Chlorinated Olefins (e.g.C_2Cl_4, C_2HCl_3)
Brominated Olefins (e.g. C_2H_3Br)
Halomethanes (e.g. CCl_4, $CHBr_3$, $CHBr_2Cl$)
Saturated polyhalogenated (e.g. $C_2H_3Cl_3$)
Pharmaceuticals (e.g. Iopromid)

Haloaromatics,
Herbicides and pesticides
(e.g. DDT, Lindane)

Dichloroethane,
Dichloromethane

Non-Halogenated Pollutants

Aromatics
e.g. BTEX

Pharmaceuticals,
Fuel oxygenates (MTBE, ETBE),
Phenols, PAHs,
Petroleum hydrocarbons

Nitro compounds
(e.g. TNT, nitrobenzene)

Lessons learnt

- The term “Nanoremediation“ needs to be extended
  - to new reaction pathways (e.g. oxidation)
  - and new contaminants (e.g. non-reducible substances)
- Fe(0)-based particles receive new exploitable properties
  - combination with other materials (e.g. Carbo-Iron, Al/Fe alloy)
- Combination of sorptive and reactive properties is beneficial
- Porous and or non-magnetic particles provide highest subsurface mobility

Thank you for your attention

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 309517