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Specific Targeting of Contaminants

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Overview

- Limitations of in-situ chemical oxidation and reduction
- Goals of Upsoil for specific targeting
- Concepts
  - Environmental conditions (temperature; oxidants)
  - Hydrophylic particles (NFe)
  - Hydrophobic coated particles (oxidants)
  - Particles in micelles (EZVI; Nfe)

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In-situ chemical oxidation/reduction

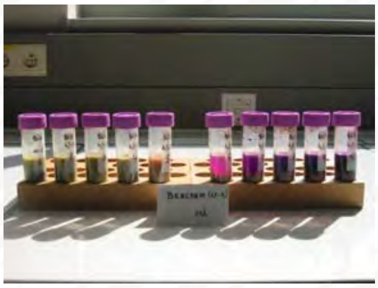
Chemical oxidants are not specific

They react not only with contaminants

But also (and even more?) with soil

Eg Fe(II)-minerals, Mn(II), sulfide, organic matter

Natural Oxidant Demand (NOD)



The same is true for **chemical reductants**, such as nano-scale particles of Fe(0)

These side reactions can vary strongly depending on the type of soil (factor 10 or more) → significant potential for cost savings

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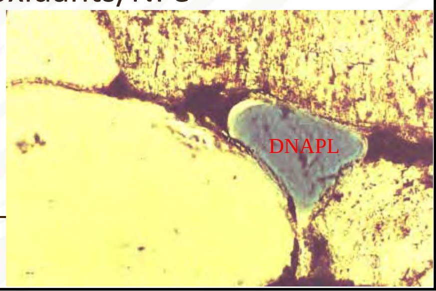
The NAPL challenge

- ISCO and ISCR-NFe is a "contact sport"
- DNAPL (pure solvent) is hard to localize in subsurface
- Conventionally oxidants and NFe are injected with water (as solution or suspenion)
- Hydrophobic NAPL does not like water (rejects it), which is bad for contact with oxidants/NFe

↓

- Modify reagents to
- improve contact with NAPL



Specific targeting

General aim:

- Develop new approaches in which oxidants/reductants will be formulated and/or applied
  - to protect them from reactions with the soil matrix and
  - to direct them to the pollutant hot spots (NAPL)
  - to allow location-specific release of the oxidant/reductant

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specific targetting

Aim: produce modified particles to/for:

- More selective oxidation/reduction
- Enhance cost-efficiency
- Lower impact on soil matrix (good for MNA)

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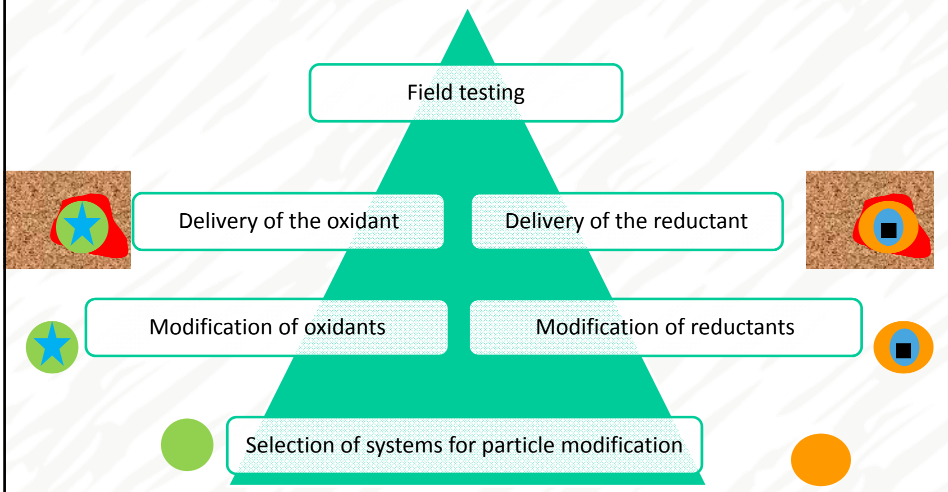
Research approach



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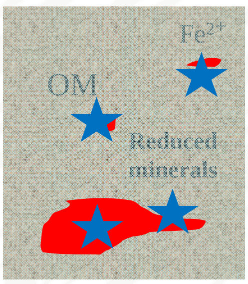
Concept 1: protection of the soil

Goal: protect organic matter & minerals in the soil



1. Temperature ↓: OM protection from oxidation

→ destruction rate of OM ↓↓;

→ destruction rate of pollutant ↓

Batch tests - rate reduction factor when T↓ (16 °C→ 4°C)

material	Permanganate	Persulphate
Peat1 (forest)	2.0-3.0	>1
Peat2 (reed)	1	<1
Oakwood	1-2	>1
Protamylasse	1-3	1 - >1
Antracite	1	No degradation
Cellulose	2.0-3.4	Limited degradation
PCE	0.5-1	No degradation, 1
Toluene	to be repeated	>1

Inject *cold* solutions in *winter time*?

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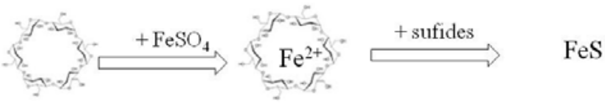
Concept 2: Hydrophilic particles

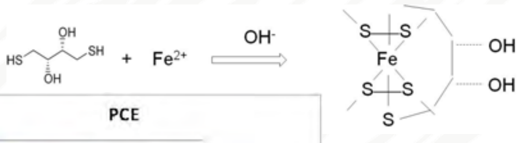
Goal: mobile, targeting particles

1. ***Cyclodextrin approach***

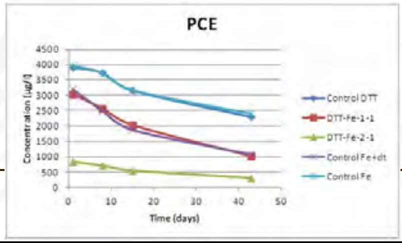


FeS kept in suspension,
but reactivity linked to FeS out of cyclodextrin

2. ***Dithiothreitol-based particles***



→ ***Reactive,***
→ ***but only at pH (11)***



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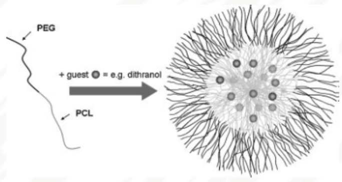
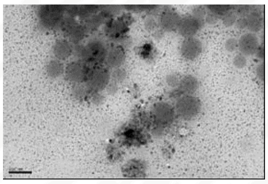
Concept 2: Hydrophylic particles

3. Polymer coated materials

3.1 Oxidants: work ongoing (ECOIND): *possible attack of the coating by oxidant?*

3.2 Reductant: coating of nano-iron with PCL-based polymers (TECNALIA)





→ Precipitates in water, nZVI in micelles? Reactivity?

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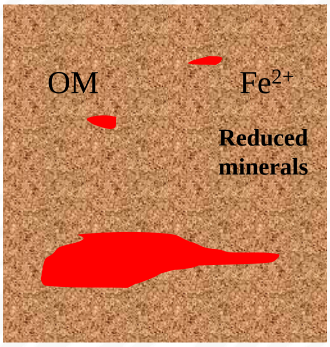
Concept 3: hydrophobic particles

Goal: mobile, targeting particles



1. Palm wax packed particles

Promising results for control of release of oxidant

2. Carnauba wax packed particles

Packed oxidants, together with Polymer Dept. of ICECHIM

KMnO4 (permanganate)

Na2S2O8 (persulfate)

Na2CO3.1/2H2O2 (percarbonate)

Results oxidant release & reactivity (next S)

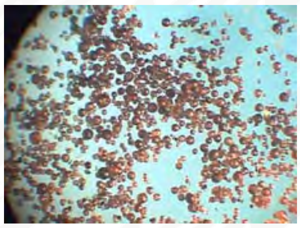
3. Mixed coated materials

ECOIND 11

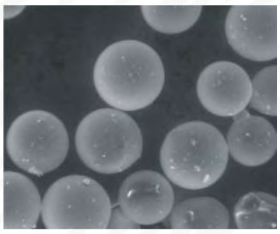
Concept 3: Hydrophobic packed particles

Permanganate packing via spray-gel congealing (*Paraffin & Carnauba wax*)

- **Step 1:**
  - *particles should stay intact in soil and in water: OK*
  - *no significant release in water (< 10% in 7 days – PROJECT target): work ongoing*
- **Step 2:** coating is soluble in organic phase
  - *Particle - coat dissolves and permanganate was released: OK!*
- **Step 3:** *oxidant reactivity?*
  - *OK for DNAPL*
  - *Partially OK for LNAPL*
  - → *OK for DNAPL-LNAPL mixtures, on long term (> 20 days)*



$KMnO_4$ – Paraffin



$KMnO_4$ – Carnauba

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Concept 3: Hydrophobic packed particles

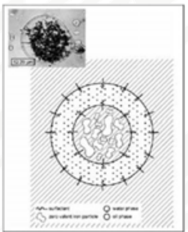
→Promising approach,

but:

→Points of attention:

- →Slow release for particles <100 µm - *not completely satisfactory yet*
- →*Packing material* or *additives* should not react with the oxidant: *OK, but restrictions on the techniques used*

Concept 4: Micelles - Emulsified reductants



Research question:

E-ZVI improves degradation of DNAPL ?

E-ZVI & E-FeS can lead to targetting?

? Degradation rates with soluble CAHs

? Degradation rates with DNAPL (residual phase)

? E-ZVI & E-FeS improved degradation icw ZVI & FeS

? Optimisation of emulsions possible?

- **First optimisation of recipe**
  - nano ZVI, micro scale ZVI, FeS, emulsion
- **Reactivity test with dissolved contaminants**
  - Emulsion reduces reactivity: Fe > E-Fe
  - Nano-iron still reactive; E-FeS much less
- **Reactivity test (column + glass beads) – DNAPL**
  - E-ZVI & E-FeS migrates better than bare materials
  - Emulsions slow down elution of DNAPL
- **Further optimisation of recipe** → one extra recipe tested
- **Reactivity test (column with sand) – DNAPL**
  - E-ZVI* migrates better than bare nZVI
  - Reactivity of nZVI maintained in column

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Conclusions

- High cost of oxidants and nano-iron → opportunity for optimized delivery → less reaction with soil, more specific for reaction with NAPL
- **Improved process conditions : temperature reduction** favours contaminant degradation over oxidation of soil organic matter
- **Hydrophylic Fe-particles:** only succesful at pH 11 (not optimal)
- **Hydrophobic packed oxidants:** some coated oxidants made with slow release of oxidant in time; further optimization for
  - very slow release up to 7 days, or
  - NO release before meeting the targeted zone
- **Emulsified nano-ZVI:** promising results with new reactive formula with improved injection properties and mobility

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