TCE AND CrVI SOURCE ZONE TREATMENT BY INNOVATIVE FORMULATION OF NZVI

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Overview

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❖ OBJECTIVES

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Currently development of **In Situ Chemical Reduction (ISCR)** using Fe(0).

Fe(0) known to **degrade lots of contaminants** (such as chloroethene, chloroethane,...) and widely used in PRB at microscale.

Fe(0) nanoscale (**NZVI**) brings:
- **Higher reactivity, Beta -elimination**
- The possibility to inject as a slurry to **treat source zone**.

NZVI is used since 10 years especially in US but only **few applications in Europe** (mostly in Germany and Czech Republic).

**NZVI technology is misread** by french institutions / administrations as no official application has been done in France yet.

Still remains societal, economics and technological obstacles.
General objective: Create NZVI emulsion able to be dispersed with a significant ROI and keeping maximum of reduction reactivity

LAB EXPERIMENTS
- **WP 1**: Stable formulation (CEREGE)
- **WP 2**: Compromise between good reactivity and slow kinetics (Univ. Aix)
- **WP 3**: Significant transfer in porous media (CEREGE/INERIS)

FIELD EXPERIMENTS
- **WP 4**: Assess ROI and reactivity with an In Situ Pilot injection (SERPOL)
WP1: Formulation

Objectives:
- Aggregation
- Emulsion stability
- Coating stability
- Coating degradability

NZVI production and technical feedbacks: AQUATEST / NANOIRON

Particle size: 20 - 100 nm

- Several coatings tested
- Good stability with CMC, Xanthan and CMC

Phenrat et al., 2008
WP 2: Reactivity

Objective: Compromise between reactivity and kinetics

- **Reactivity in GW**: Complete removal of 10mg/l TCE for the 3 coatings but with different kinetics
- Very low daughter products production (150 µg/l cis-DCE and <10µg/l VC !) => Mainly β-elimination pathway
WP 2: Reactivity

- Reactivity with soil and GW:
  80% TCE degradation after 35 days with PAA coating

- NZVI lifetime > 35 days

- PAA is the best candidate to maintain NZVI reactivity as long as the particle is mobilized from injection well

- Complementary studies on competitors effect ($\text{SO}_4^{2-}$, $\text{CrVI}$, $\text{NO}_3^-$, $\text{HCO}_3^-$, ...) needed
WP 3: Transfert

**Objective:** Best transfer in porous media

- No migration of non coated NZVI
- Significant migration of coated NZVI through sand model

Limited but effective transfer of coated NZVI through site sediment

Coated NZVI

Bare NZVI

Tracer (NaCl)

SAND MODEL

SITE AQUIFER (Gravel and sand)

Kumar et. al, 2012 (unpublished data)
WP 4: In Situ Pilot Injection

- **History:**
  - Surface treatment factory
  - TCE pit and Chromium acid baths
  - Leak suspicion

- **Contamination:**
  - Mixed pollution CrVI and TCE
  - Downstream impacts
  - Well identified CrVI and TCE source zone

- **Hydrogeological studies:**
  - Groundwater velocity: 1-2 m/day
  - Sand and gravel geology
WP 4: In Situ Pilot Injection

Hydraulic barrier to:
- stop pollutant migration downstream
- prevent potential NZVI migration
WP 4: In Situ Pilot Injection

[TCE]_{GW} = 600 - 4500 \mu g/l
[TCE]_{soil} : some mg/kg

[CrVI]_{GW} = 1700 - 18000 \mu g/l
[CrVI]_{soil} = 15-50 mg/kg
WP 4: In Situ Pilot Injection

French administration to convince that NZVI inherent risk is controlled!!

Safety measures

- **Transport**: NZVI slurry stabilised by nitrogen to reduce risk
- **NZVI handling by operators / Specific protection**: glasses, type of gloves, specific suit and mask
- **Waste management**: quick NZVI oxidation and aggregation when exposed to air / no specific regulation
- **Tasks and risks analysis for NZVI injection**: all different steps during injection operation are described and inherent risks are analysed to manage any risk
WP 4: In Situ Pilot Injection

Pilot injection phases

- **First phase (July 2012): Estimate ROI**
  - 1 well injection (S3)
  - 1g/l PAA coated NZVI
  - 10 kgs total NZVI injected

- **Second phase (March 2013): Treat TCE and CrVI source zone**
  - 3 wells injection (S1, S2, S3)
  - 2-3 g/l PAA coated NZVI
  - 30 kgs total NZVI injected
WP 4: In Situ Pilot Injection

MONITORING
- pH, Eh, conductivity
- COHV
- CrVI
- CrIII
- TOC
- Electron acceptors: $O_2$, $NO_3$ et $SO_4$
- End products: Ethene / Ethane / Chloride
- Bromide
- Particle size / oxidation state

Injection wells
WP 4: In Situ Pilot Injection

Conceptual scheme

Half-inch diameter of piezometer
• **1st injection:**
  - ROI between 2.5 and 4m (visual appearance of NZVI)

• **2nd injection:**
  - Strong redox decrease (down to – 700 mV !)
  - Oxygen decrease
  - pH increase (2.5 unit increase up to pH 9.8)
WP 4: In Situ Pilot Injection

- After 2\textsuperscript{nd} injection: TCE concentration below 150 µg/l for the 3 wells in source zone (no rebound yet)
- No daughter compound at all (difficulty to assess what is due to degradation/dilution + mass balance)
WP 4: In Situ Pilot Injection

- **1\textsuperscript{st} Injection**: two phenomenon observed:
  - flushing of CrVI downstream (S1 after 1\textsuperscript{st} injection)
  - reduction in CrIII close to injection well (S2)

- **2\textsuperscript{nd} injection**: total CrVI decrease at this step
Conclusions and perspectives

- **Satisfactory compromise** in lab between **emulsion stability, reactivity** and **mobility** with PAA coating

- On field, satisfactory **ROI between 2,5 and 4 m** (ROI theoretical 5m) but no information on vertical distribution

- Competitors effect has to be studied to define the frame where NZVI can be applied

- TCE and CrVI reduction on source zone has to be confirmed during next weeks

- Technical and economic study on NZI application has to be done to define the relevant frame for using NZVI
Thank you for your attention!!