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Planning of a Nano-Remediation:

From Mobility and Reactivity Lab Tests to Field Applications

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Groundwater Remediation using Nano Zero-Valent Iron (nZVI)

In-situ chemical groundwater remediation technology for source and plume treatment in the saturated zone.

Introduction of nZVI (one or more dimension less than 100 nm) as aqueous slurries into subsurface is possible via injection well or with the direct push method.



Mobility Experiments:

A stable suspension of 10 g/L nZVI and 10 g/L CMC is continuously mixed in an anaerobic system (1-3) and injected (q=0.91 m/h) into a sand filled column (5,7). mixing reservoir
temperature sensor
disperser
a inflow sampling valve
b outflow sampling valve
peristaltic pumps
pressure transducer
column filled with porous media
movable magnetic susceptibility sensor
discharge sample
scale
controlling and measurement device



The dissolved contaminant is degraded by a reductive dehalogenation on the surface of the nZVI.



 $C_2Cl_4 + 4Fe^0 + 4H_2O \rightarrow C_2H_4 + 4Fe^{2+} + 4Cl^- + 4OH^-$

During injection liquid samples are collected at the inflow and outflow $\begin{bmatrix} 1 \\ 1 \\ (4a,b) \end{bmatrix}$ and pressure (6) and mass flux $\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$ (9,10) are continuously measured.

The distribution of nZVI inside the column as a function of time and space, can be determined with the non-destructive magnetic susceptibility measurement.

Reactivity Experiments:

e W = 16 W = 16 W = 14 V = 14



After injection of nZVI dissolved PCE (c_{PCE} =100 mg/L) is injected for 84 days (q=0.007 m/h) into the columns (15, 16, 17).

PCE, TCE, chloride, gaseous parameters, metabolites, pH and ORP are measured continuously (7,18,19,20).









In order to design an efficient and economical nZVI remediation it is crucial to combine the two complex topics: Mobility and Reactivity.

Thus, experiments adequately describing particle distribution and degradation efficiencies have to be designed and conducted.

magnetic valve (MV extra) 14 overflow container -tap water globe valve for sampling 15 contaminant (PCE) solution three-way globe valve 23 16 syringe dosage system magnetic valve (MV) 17 columns filled with sand and nZVI degassed H₂O 6 three-way globe valve 18 gas traps Ar for injection and sampling 19 cont. pH & redox measurement 20 outflow bottle 7 three-way globe valve 21 detection of online for sampling pH & redox measurements water degassing unit 22 PC controlling LOGO and 9 argon supply 10 membrane pump (EMP) syringe dosing unit 23 controlling system of the MVs (LOGO) 11 sand filter 12 water reservoir 21 l-e-i ______

In order to determine particles longevity $(t_{1/2})$, nZVI inside the columns is determined with the magnetic susceptibility sensor in defined time intervals.

Degradation efficiencies (η), degradation kinetics, and corrosion are calculated with mass balances from sampling results.

Particle	L	n	m _{ZVI,t0}	m _{ZVI,t36}	t _{1/2}	m _{PCE,in}	m _{PCE,deg}	η_{PCE}	η _{CI-,PCE}	$\eta_{Ethene,Ethane}$	η _{cor}
	[m]	[-]	[g]	[g]	[d]	[g]	[g]	[%]	[%]	[%]	[%]
STAR	1.9	0.4	6.0	0.6	25.7	1.5	0.56	37.5	24.5	11.4	84.4
25DS	1.9	0.4	8.5	5.6	173.3	1.6	0.84	53.8	74.4	42.9	34.1
25DS ORM	1.9	0.4	6.1	4.7	231.0	1.6	0.82	49.8	61.9	23.2	30.2



nZVI particles (M_{ZVI} = 55.85 g/mol, ρ_{ZVI} = 7874 kg/m³)

NANOFER STAR: powder, 77 % ZVI, 23 % iron oxides, $d_{50} = 50 \text{ nm}$, BET = 25-30 m²/g

NANOFER 25 DS: concentrate, 80 % water, 20 % iron (70 % ZVI, 29 % magnetite, 1 % iron sulphide), pH 11-12, d₅₀ = 50 nm, BET 25-30 m²/g

NANOFER 25 DS ORM: NANOFER 25 DS + surfactant

Stabilizer

Polymer sodium carboxymethyl cellulose (CMC): white powder, water soluble thickening agent, water binding properties, increases viscosity

Water:

Degassed tap water ($O_2 \le 1.5 \text{ g/L}$)





The distribution of the particles decreasing exponentially, best distribution for 25DS, worst for 25DS ORM.

Distribution and thus, amount of nZVI can influence the degradation. The addition of sulphide to the ZVI particles improves the particle mobility.

Best degradation for 25DS particle.

The addition of sulphide to the ZVI particles increases the degradation efficiency of PCE, accelerates the full degradation pathway to the end products chloride and ethene/ethane, increases the longevity and reduces corrosion.