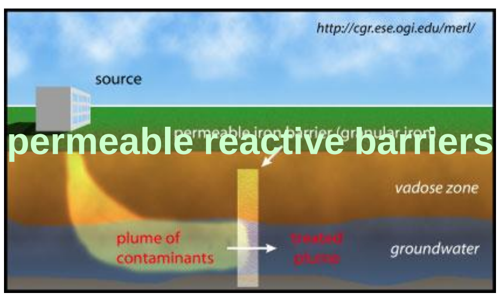
Labex Serenade

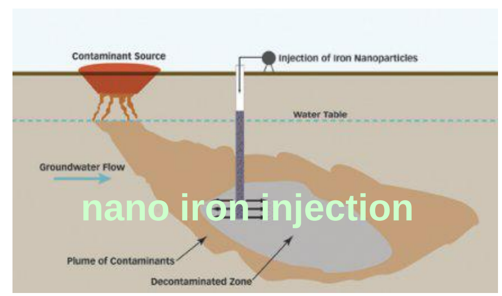
Groundwater pollution treatment with micro and macro ZVI compared with nano ZVI

NanoFreze

250000 polluted sites

5000 polluted sites





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- Elettra Synchrotron Lightsource at Trieste (Italy)
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Fe° Permeable Reactive Barrier Technology

Within the last 20 years the iron wall technology has developed to a standard technology for groundwater remediation and wastewater treatment with worldwide acceptance. Fe° PRB is regarded as **a reductive technology** for organic contaminants, for inorganic contaminants, **reductive precipitation** (Gu et al., 1998, Puls et al.,1999), **co-precipitation** (Lackovic et al., 2000, Paspaliaris, 2006, Noubactep et al., 2006) and **adsorption** onto iron oxides and oxy-hydroxides are considered as **major reaction paths**(Henderson and Demond, 2007, Johnson et al., 2008, Silvia Comba, 2011).

PRB systems are using wide range from 20 to 100 vol% of Fe^0 depending upon contaminants and level of treatment required

The reactivity of Fe°

The Evolution of Fe phases

Fe° > $Fe(OH)_2$ > Fe_3O_4 > γ-Fe_2O_3 or γ-FeOOH and also due to the strong increase of sulfate and nitrate reducing bacteria:

mackinawite ((Fe,Ni)1 + xS (where x = 0 to 0.11)) or amorphous FeS which increase the oxidation rate of Fe° and play a role in the sorption/incorporation of metals

Current limitations:

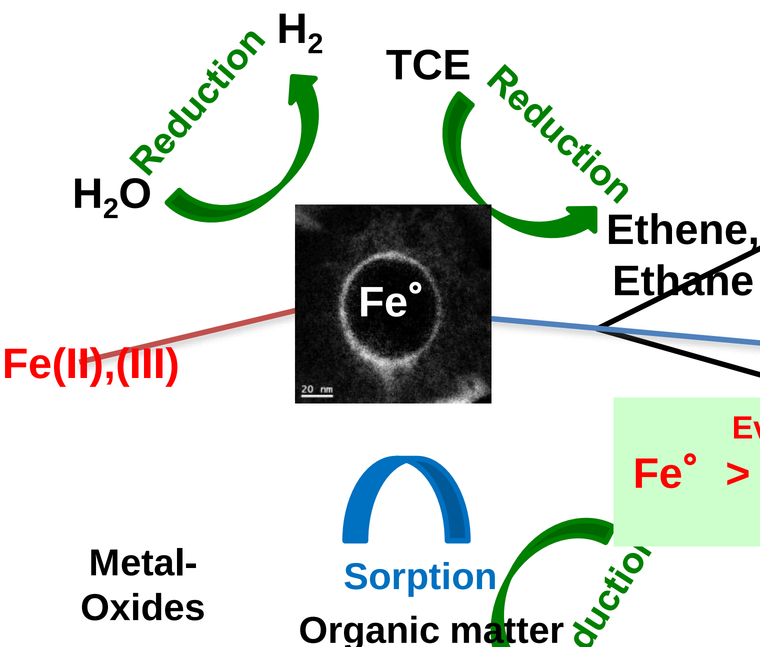
(i) the longevity of the wall in terms of Fe^0 reactivity loss, resulting from the build-up of mineral precipitates at the Fe^0 surface is not fully understood
(ii) Evolution of microbial population in PRBs and Reactive Zones, and their interaction with contaminants and Fe^0 particles
(iii) Oxidation and transport of iron nanoparticle in porous media.

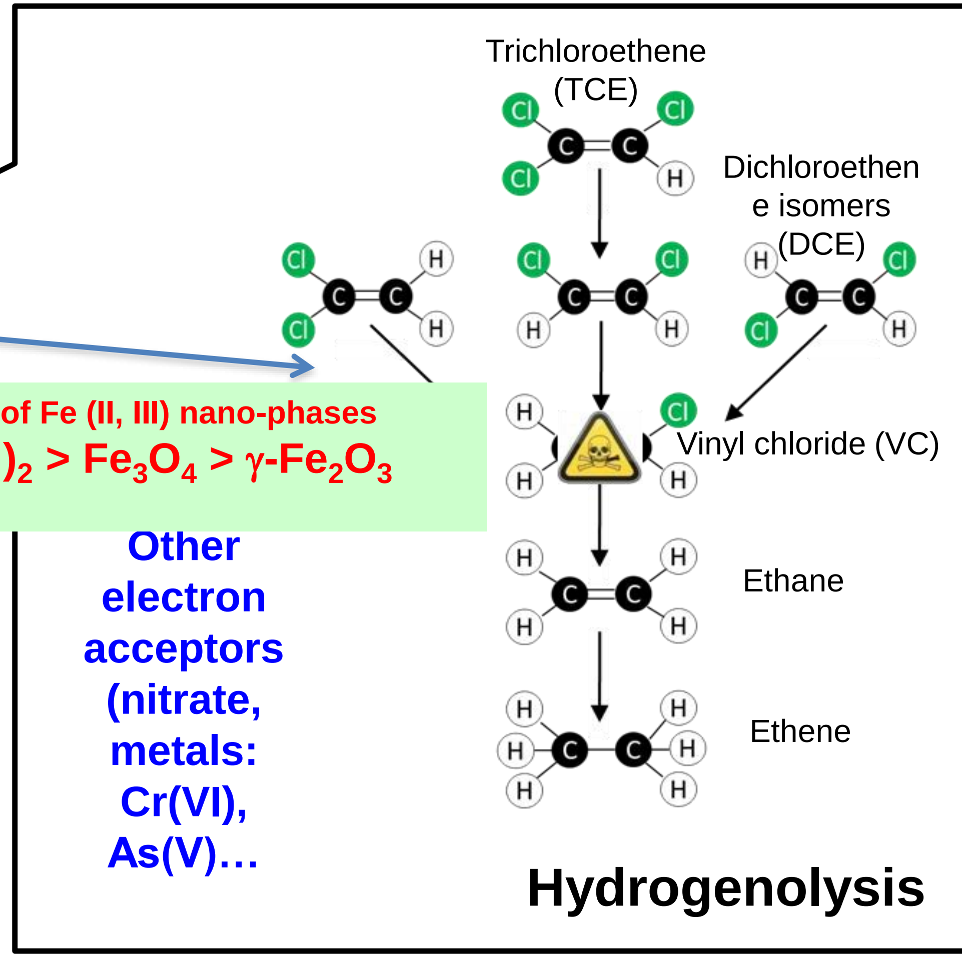
N Kumar PhD Thesis 2014

Nano ZVI for underground water treatment

Same activity as micro and granular Fe° = reduction, adsorption…

- **Redox reactions involved**

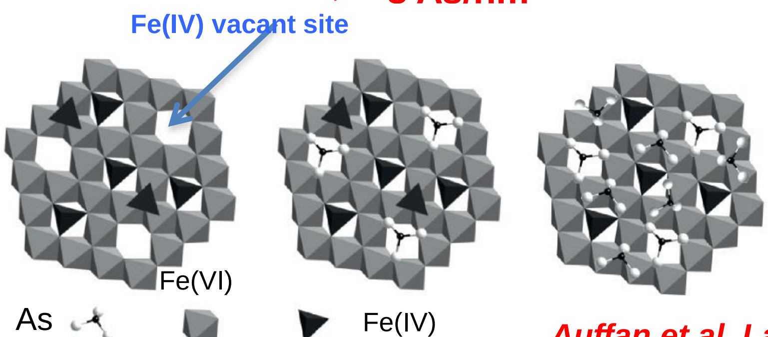




Evolution of Fe (II, III) nano-phases

Fe° > $Fe(OH)_2$ > Fe_3O_4 > γ-Fe_2O_3

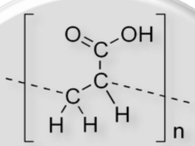
But well known Higher reactivity of γFe_2O_3 for As(III) adsorption
=> ~8 As/nm²



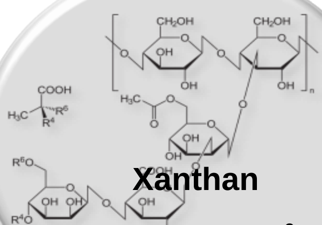
Auffan et al, Langmuir 2008

Nano ZVI: Efficiency depends on: 1-porous media complexity, 2- Coating

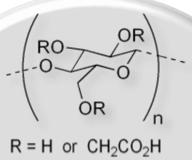
1- The transfer of NanoZVI within the porosity of a real sediment: surface functionalisation



PAA
PolyAcrylic Acid
M.W. = 1,8.10³ g.mol⁻¹

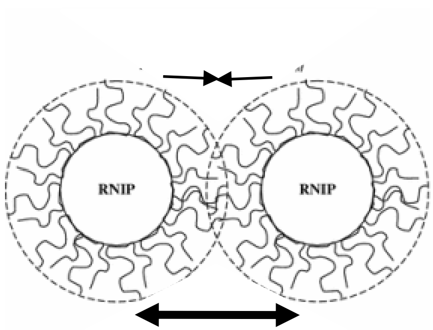


Xanthan
M.W. = 4,0.10⁶ g.mol⁻¹

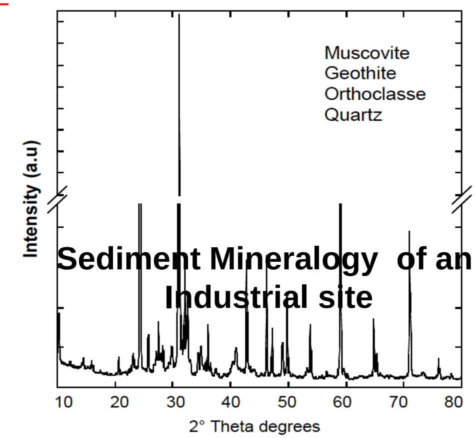


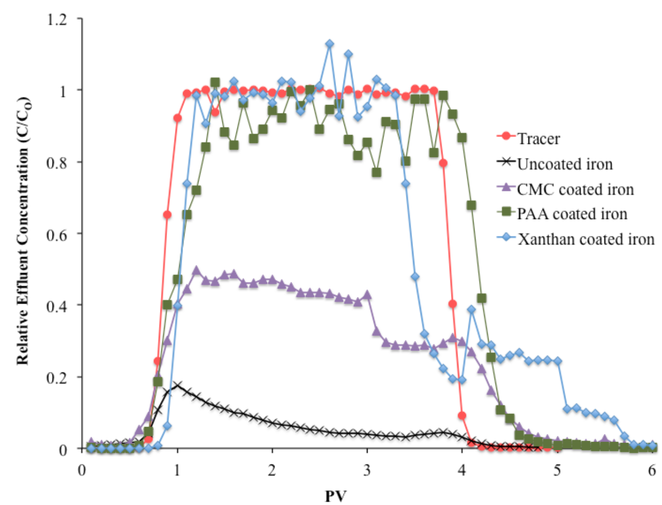
CMC
CarboxyMethylCellulose
M.W. = 9,0.10⁴ g.mol⁻¹

Coated NZVI



Phenrat et.al 2008



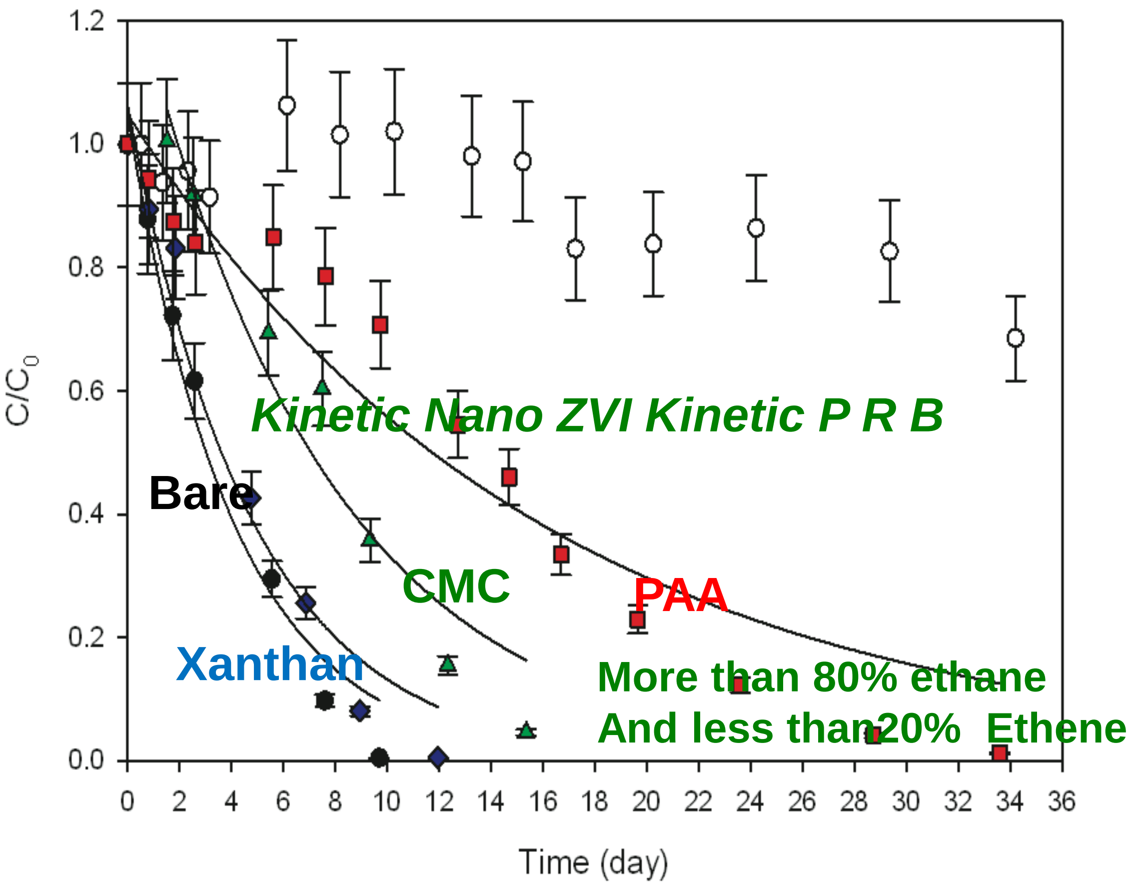


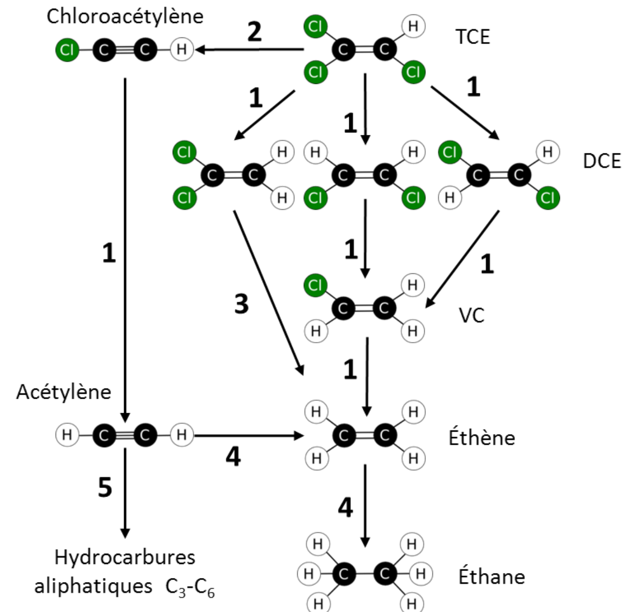
Attachment efficiency: probability to sorb onto sediment
For Coated nFe° : α = 0.240 for Xanthan and PAA
For uncoated nFe° = α =0.88

Kumar et al ES and T 2015

2-Effect of coating

- Removal of TCE and rate constants:



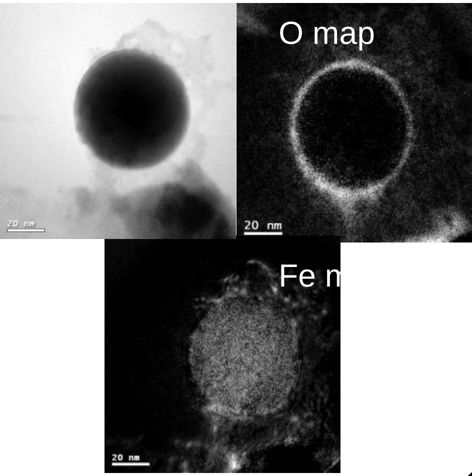


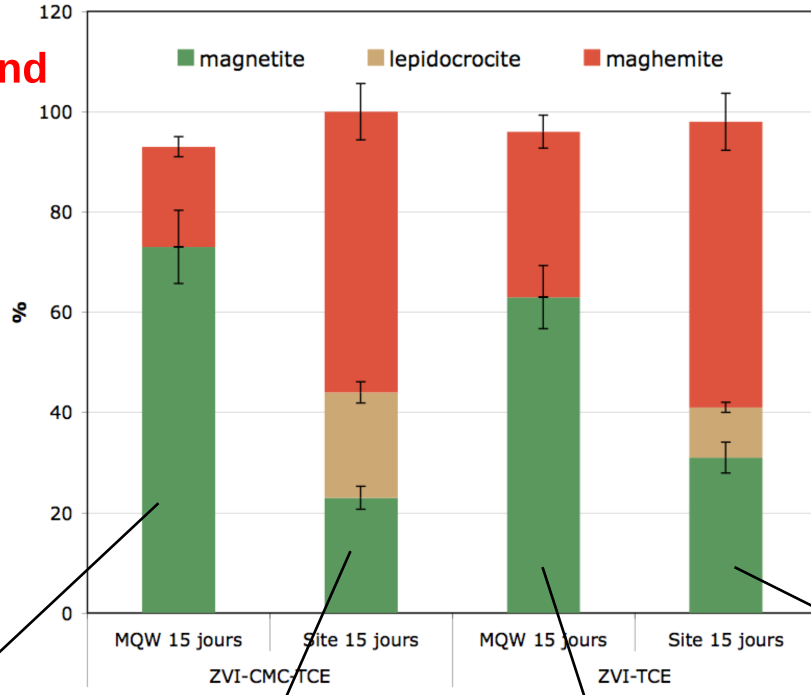
Pseudo-first order kinetic :
$$C/C_0 = e^{-kt}$$

NZVI	k_{obs} (h^{-1})	r^2	Time for 100% removal (d)
Bare	0,0145	0,955	~ 10
Xanthan	0,0087	0,969	~ 12
CMC	0,0056	0,942	~ 19
PAA	0,0026	0,925	~ 34

Complete removal between 10 and 34 days

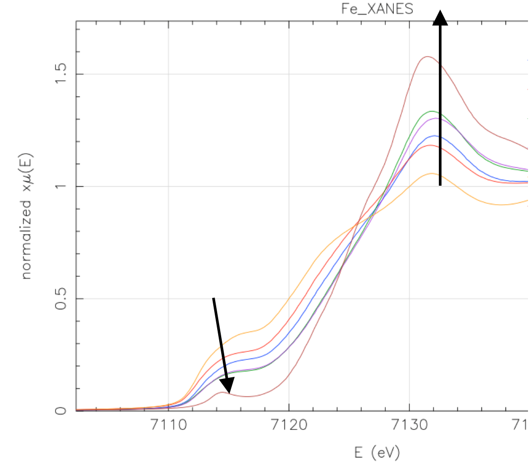
Oxidation Mechanisms and Kinetic comparison with industrial site water: XANES and TEM data

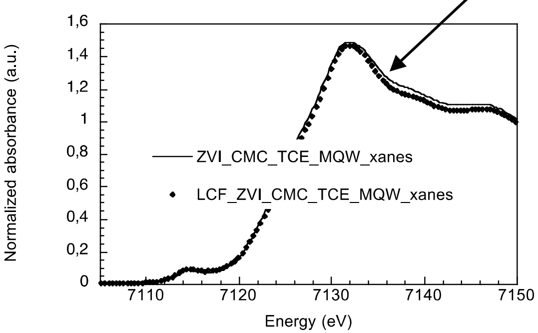


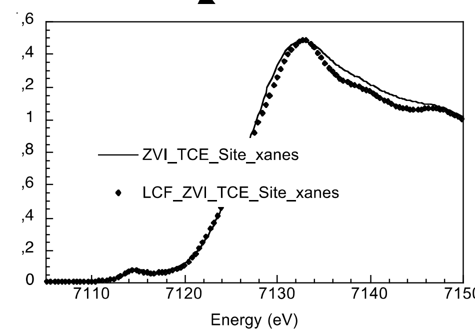


Coated

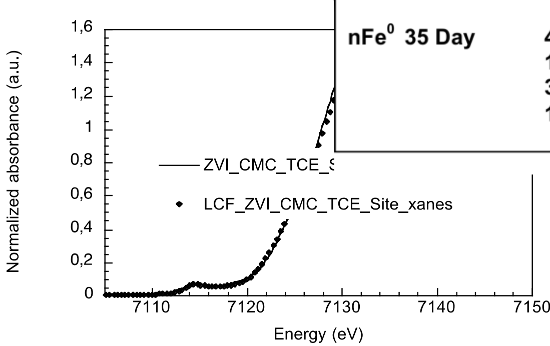
Uncoated

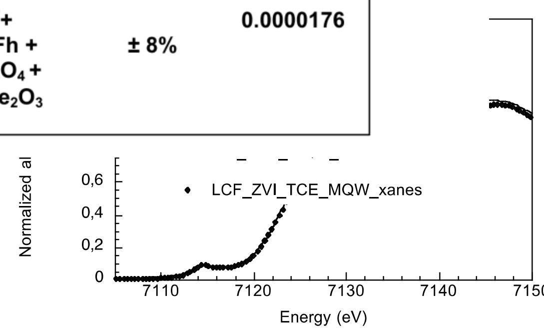






sample	mineralogical composition	% of error	residue χ^2
nFe^0 initial	85% Fe^0 + 16% Fe3O4	± 8%	0.000053
nFe^0 7 Day	69.5% Fe^0 + 30.6% Fe_3O_4	± 8%	0.0000612
nFe^0 14 Day	39% Fe^0 + 16% 2LFh + 44% Fe_3O_4	± 8%	0.0000452
nFe^0 35 Day	40% Fe^0+ 18% 2LFh + 30% Fe_3O_4 + 11% γ-Fe_2O_3	± 8%	0.0000176





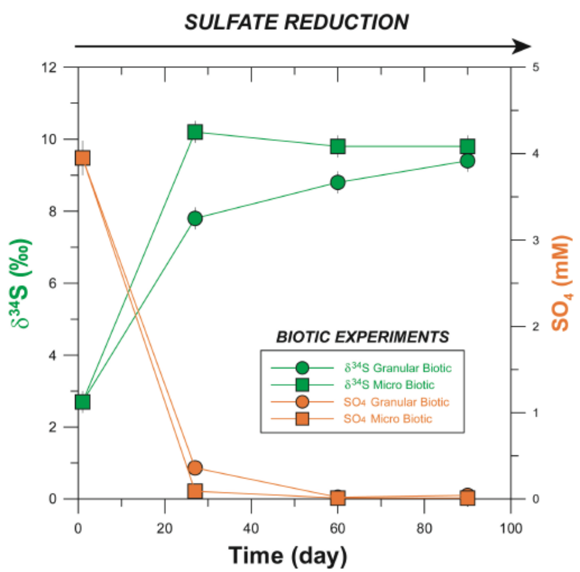
Differences in terms of bio-activity vs size of Fe° evaluated using materials from polluted industrial site (microcosm and column experiments)

S.No		Concentration
1	pH	4.1
2	ORP	326 mV
3	EC	987 µS cm^{-1}
4	Dissolved oxygen	0.13 mg L^{-1}
5	Dissolved Sulfate	420.00 mg L^{-1}
6	Zinc	49.00 mg L^{-1}
7	Cadmium	0.41 mg L^{-1}
8	Fe	7.48 mg L^{-1}
9	As (Total)	0.04 mg L^{-1}
10	Chloride	21.00 mg L^{-1}
11	Nitrate (as Nitrogen)	1.00 mg L^{-1}
12	Total hardness	2.40 mmol. L^{-1}
13	Total Organic carbon	2.70 mg L^{-1}

Table: 3.1: Groundwater characteristics

S.No		Concentration
1	pH	4.18
2	Total Organic carbon	0.02
3	Total S (mgS/Kg)	219.00 (mg Kg^{-1})
4	Mn	16.00 (mg Kg^{-1})
5	Fe (mg/Kg)	650.0 (mg Kg^{-1})
6	Cd (mg/Kg)	0.60 (mg Kg^{-1})
7	Zn (mg/Kg)	41.00 (mg Kg^{-1})
8	As (mg/kg)	75.00 (mg Kg^{-1})

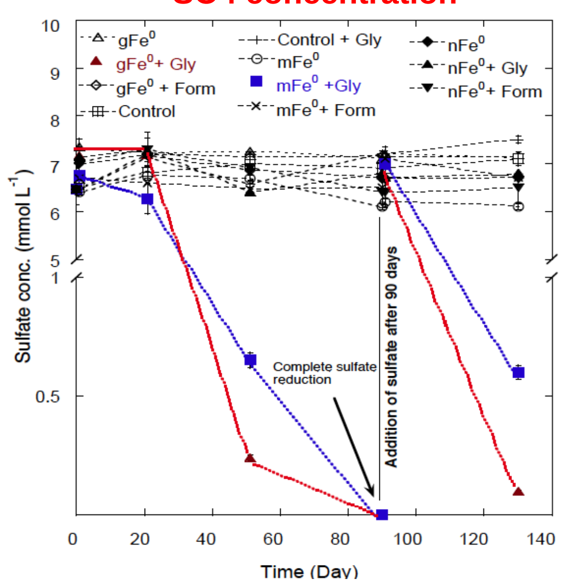
Table: 3.2: Sediment Characteristics

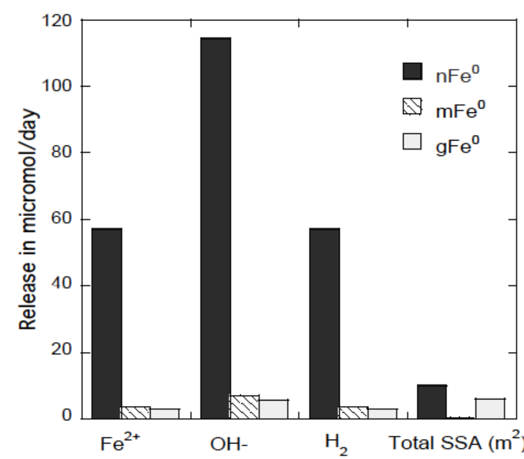


Comparison of dissolved SO_4 and $d^{34}S$(%) vs time for biotic columns showing the activity of SRB (Sulfate Reduction Bacteria)

Nano ZVI do not decrease SO4 concentration

Chapter 3: Stimulation and inhibition of SRBs by Fe⁰: a batch study





Release of Fe^{2+}, OH^- and H_2 vs size of Fe° (n= nano, m= micro, g= granular) in glycerol amended microcosm

Kumar N Water Res 2014 and Chemosphere 2013

Conclusion

In the presence of nFe^0, no sulfate reduction was observed, although the results obtained with gFe^0 and mFe^0 microcosms confirmed the presence of SRB species in the aquifer sediment, and the pH and ORP conditions were favorable. A possible explanation for this observation could be the bactericidal properties of nFe^0 which have been previously linked to the (a) reduced state of particle, (b) cell membrane disruption, (c) Fe^{II} induced generation of reactive oxygen species, or (d) a combination of all of these (Lee et al., 2008, Auffan et al., 2008).

Nano ZVI is useful for treating the underground polluted waters due to
-Large production of H_2 electron donor
-Possibility to coat differently from site to site to transfer
-The adsorption of reduced As is larger with nano ZVI than m or g Fe° because reactivity of As(III) for nano Fe oxides is >>> than for Fe..S

We thank also

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Any Questions?