Trap-Ox Fe-zeolites for in-situ trap&treat of organic contaminants: lab-scale results on mobility, performance and stability

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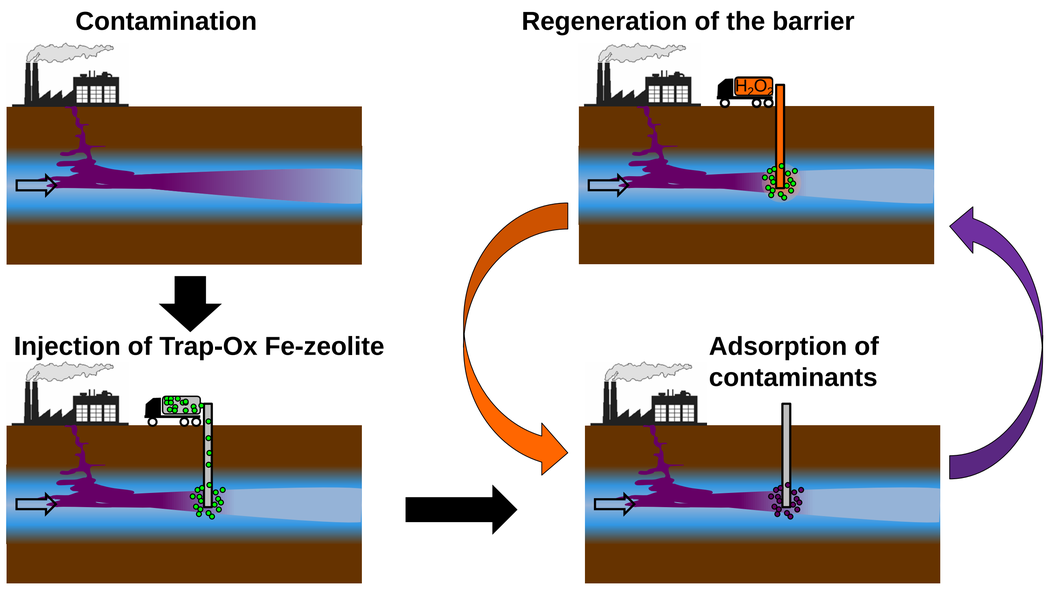
Concept

Trap-Ox Fe-zeolites were developed within NanoRem as particles for in-situ chemical oxidation (ISCO). Fe-zeolites are active Fenton-like catalysts for production of OH-radicals even at neutral pH and additionally act as adsorbents for organic contaminants. Thus, injection of Fe-zeolite suspensions into the aquifer can be used to

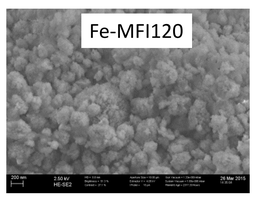
I) install a sorption barrier to *trap* dissolved contaminants and prevent further spreading of plumes and to

II) *oxidize* and thus degrade adsorbed contaminants by injection of H_2O_2 for regeneration of the adsorbent. These adsorption/oxidation cycles can be repeated if required.



Suspension stability and transport properties

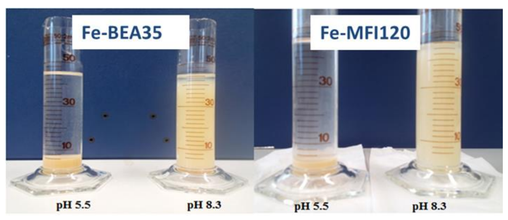
SEM images of Trap-Ox Fe-zeolite powders



Trap-Ox Fe-zeolite type	Max. pore diameter [nm]	Molar ratio SiO_2/Al_2O_3 [-]	Fe content [wt%]	Zeta potential [mV] [1]	Particle size [nm] [1]
Fe-BEA35	0.75	35	1.3	-30	550
Fe-MFI120	0.56	120	0.3	-28	840

[1] Zeta potential and average diameter determined by DLS in very hard water (F.I.h, pH 8.5)

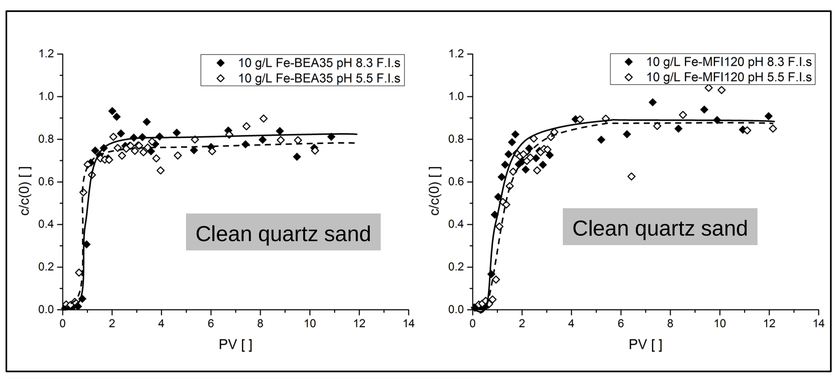
Suspension stability (24 h, 10 g/L Trap-Ox Fe-zeolite at pH 5.5 and 8.3)



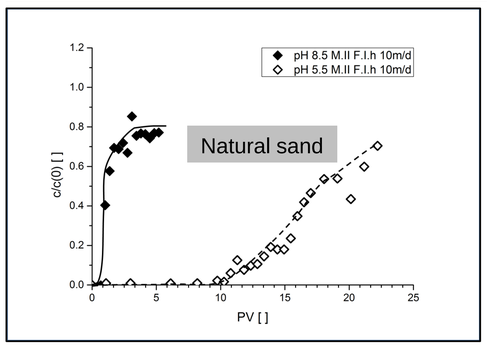
Two Trap-Ox Fe-zeolite particle types were studied in detail within NanoRem, differing in hydrophobicity and pore size: Fe-MFI120 as high-performance adsorbent for small organic contaminants and Fe-BEA35 which is applicable for a wider contaminant spectrum due to larger pores.

Suspensions of Trap-Ox Fe-zeolites adjusted to slightly alkaline conditions (pH 8 to 8.5) are very stable even at high particle concentration (10 g/L) without any additional stabilizers.

Mobility in column tests – influence of pH and porous medium



- 10 g/L Trap-Ox Fe-BEA35
- I = 20 cm
- flow velocity: V_{eff} = 10 m/d
- water: EPA standard: soft (F.I.s) or very hard (F.I.h)
- porous media:
  - clean sand (M.I Dorsilit, acid washed, 0.3 - 0.8 mm)
  - natural sand (M.II)



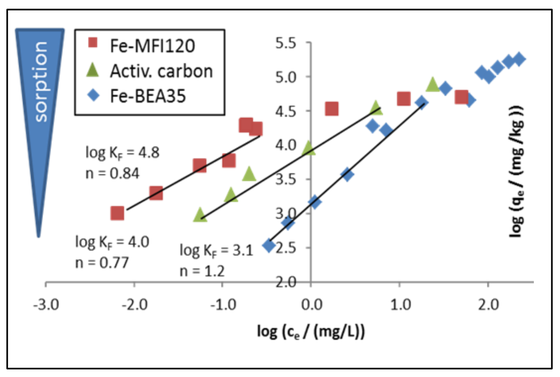
Both Trap-Ox Fe-zeolites show high mobility irrespective of pH in cleaned quartz sand.

In native sand breakthrough occurs in a blocking type behaviour at acidic pH due to attractive electrostatic interactions between negatively charged particles and positvely charged iron oxides.

For optimal mobility, Trap-Ox Fe-zeolites are applied in suspension with slightly alkaline pH without the need of additional stabilizers.

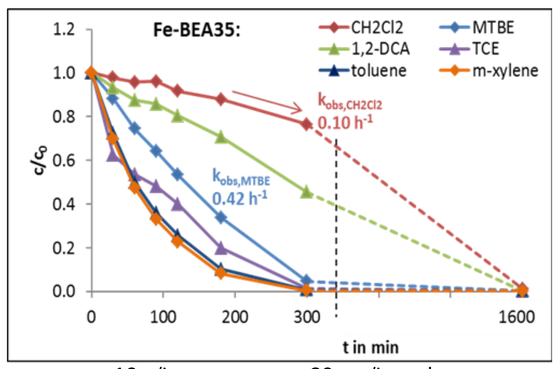
Adsorption and catalytic oxidation of contaminants

Freundlich plot of MTBE adsorption isotherms



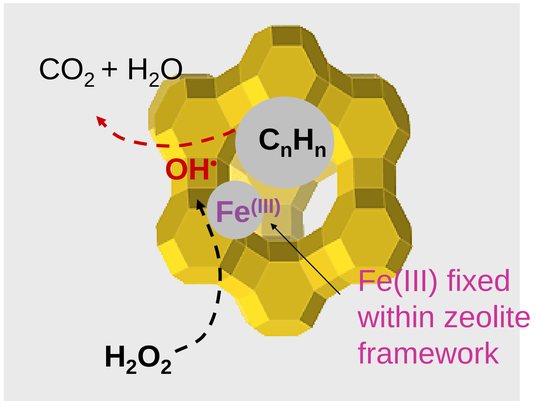
Fe-MFI120 shows high performance even outcompeting activated carbon (AC) in adsorption of small organic contaminants such as MTBE at low concentrations (< 10 mg/L).

Degradation of adsorbed contaminants with H_2O_2



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

Fenton-like oxidation



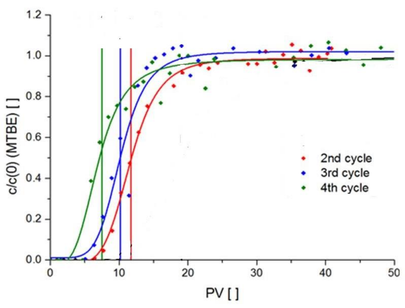
OH-radical driven oxidation degrades a wide range of organic contaminants including those not amenable to reduction by Fe^0-based nanoremediation particles (e.g. 1,2-dichloroethane (1,2-DCA) and dichloromethane (CH_2Cl_2)).

Fe-zeolites are active at a wide pH-range (pH 3 to 8.5) eliminating, avoiding additional reagents (acids or complexants as applied in conventional in-situ Fenton treatments).

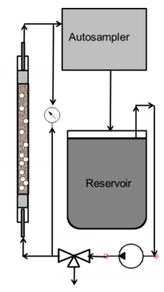
Stability under field-like conditions

Sorption/oxidation column test with Trap-Ox Fe-BEA35 infiltrated into sand

MTBE retardation factor = 8…12 at 0.25wt% zeolite loading, maintained over 4 cycles of sorption/oxidation



- clean sand (M.I Dorsilit, acid washed, 0.3 - 0.8 mm) in 20 cm column
- water: EPA standard very hard (F.I.h, pH 8.3)
- **Injection**: F.I.h + 10 g/L Trap-Ox Fe-BEA35, V_{eff} = 10 m/d → loading on sand 0.25wt% finally
- **Adsorption**: F.I.h+ 10 mg/L MTBE, V_{eff} = 1 m/d
- **Oxidation**: F.I.h + 10 g/L H_2O_2



Changes in composition, adsorption and catalytic activity after ageing of Trap-Ox Fe-BEA35 in very hard water (F.I.h, pH 8.5) with NOM (7.5 mg/L) for 38 d with 11fold exchange of water phase and a solid water ratio of 1:10

Property	Trap-Ox Fe-BEA35 **fresh**	Trap-Ox Fe-BEA35 **aged**
Fe [g/kg]	16.2	15.8
Ca [g/kg]	0.34	5.5
Mg [g/kg]	< 0.3	12
Molar ratio SiO_2/Al_2O_3	34	31
Molar ratio (Fe + Mg + Ca)/Al	0.33	1.1
Specific surface area [m^2/g]	627	634
$K_{d,MTBE}$ (at $C_{free,MTBE}$ = 6–7 mg/L) [L/kg]	1200	900
A_{MTBE} [L/kg/h] ($C_{Fe\text{-}zeol.}$ = 50 g/L, C_{MTBE} = 500 mg/L, 8–10 g/L H_2O_2, pH = 8.3–8.5; medium: F.I.h)	12	1.2
A_{TCE} [L/kg/h] ($C_{Fe\text{-}zeol.}$ = 7–9 g/L, C_{TCE} = 100 mg/L, pH = 8.3–8.5; medium: F.I.h.	140	52

Major changes during ageing involve uptake of divalent cations (Ca^{2+} and Mg^{2+}). No significant changes in specific surface area and Fe content.

Adsorption of MTBE remains high. The Fe-zeolite remains active as catalyst for contaminant degradation, however, at a lower reaction rate. The loss in activity depends on the target contaminant.

Summary and Conclusions

Optimized Trap-Ox Fe-zeolites extend the application range of nanoremediation towards non-reducible + hardly biodegradable contaminants.

They form stable suspensions and are sufficiently mobile without additional stabilizers and thus are suitable for injection by direct push or well infiltration.

Trap-Ox Fe-BEA35 is active as adsorbent and Fenton-like catalyst for contaminant oxidation with H_2O_2 even in very hard, slightly alkaline groundwater (pH 8.5) containing NOM. It can be anticipated that Trap-Ox Fe-BEA35 remains active within a period of at least two months under these ‘worst case’ conditions. During this period Trap-Ox Fe-BEA35 can trap (eliminate) dissolved contaminants and allows catalytic oxidation of adsorbed contaminants. The lifetime of Trap-Ox Fe-zeolites at specific site conditions needs, nevertheless, to be evaluated in experiments with on-site groundwater.

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

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