ATV Temadag 1. Soil Mixing som afværgemetode
4. marts 2019
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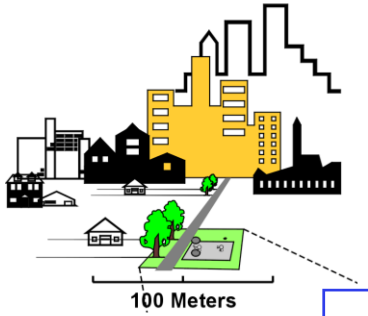
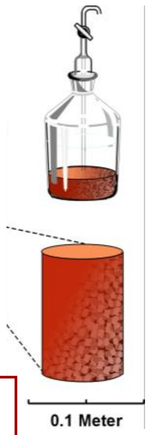
Nuværende vidensniveau omkring reaktanter

Hvordan udvælges reaktanter og hvad skal man være særligt opmærksom på

Knowledge level





Tested - field

ISCR
(clay, no cement)

Zero valent iron (ZVI)

High CVOC removal
Metals (Cr^{VI}), nitroaromatics

ISCO
(w/wo cement)

Persulfate
Permanganate
Peroxide

High CVOC and BTEX removal
Pesticides, PAHs

Mainly 2-step approach
(1) Removal (2) Strength

1-step approach

<u>Alternatives:</u>
Hot air
Sorbent
Bioenhancement

Development - lab

ISCR
(w. cement)

Fe^{II} salts
ZVI species
Fe^{II} minerals

High CVOC removal

ISCO
(w. cement)

Persulfate

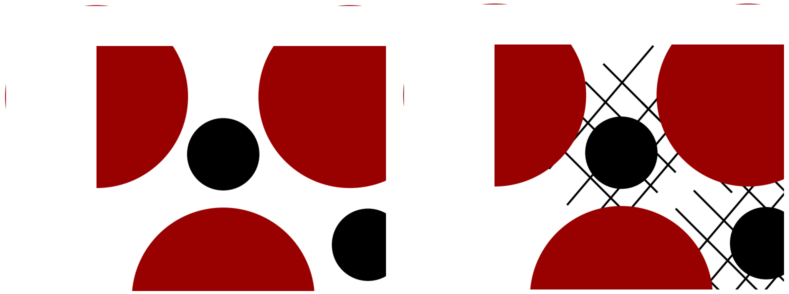
Good BTEX removal
Some PAHs

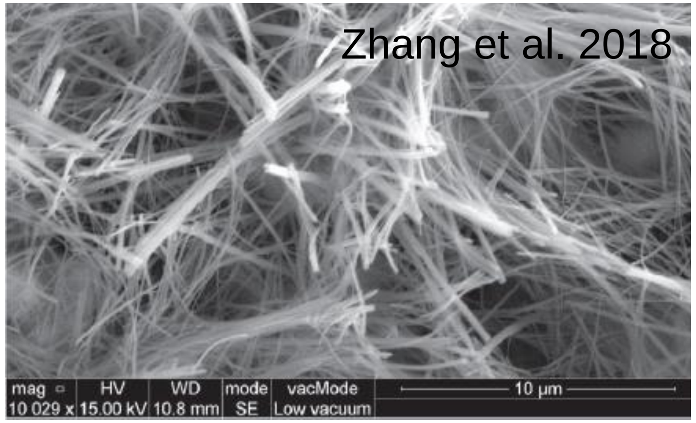
Reactive environment:

Awareness on interferences vs synergies

- ISS binders: **Portland cement** (blast furnace slag, flyash, lime, bentonite)

- Important hydration/curing processes:
  - – Loss of moisture
    - Degradation processes occur in the water phase
  - – Reduced porosity/conductivity
    - Leaching reduced
    - Reaction processes can become diffusion controlled
  - – Rise in temperature
    - Generally increase chemical reaction rates (and desorption)
  - – **Increase of pH**
    - High pH can be either facilitate or inhibit reaction (reactant dependent)

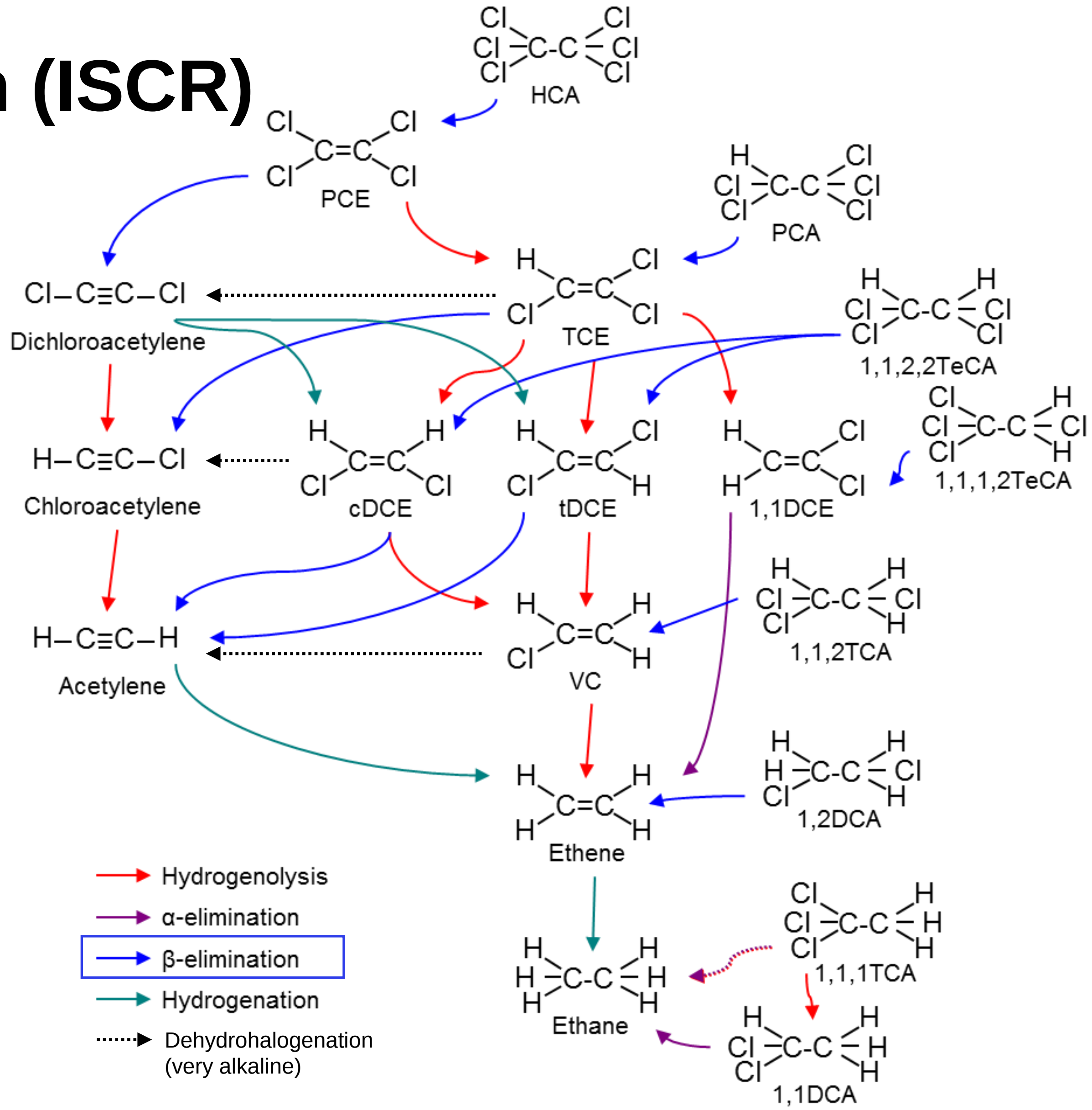




Zhang et al. 2018

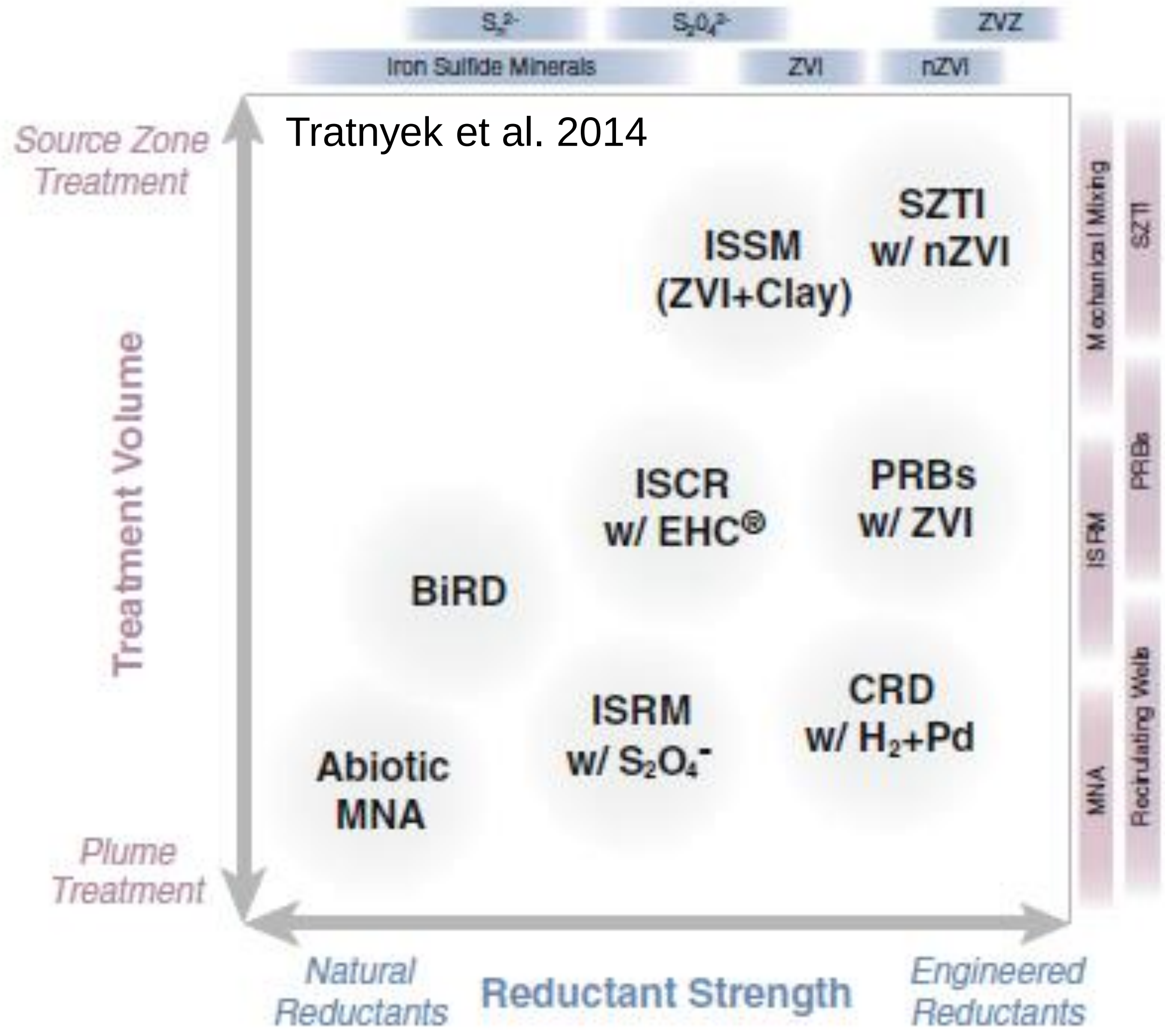
In situ chemical reduction (ISCR)

- Degradation by electron transfer from the reductant to the contaminant
- Contaminants with a desirable reductive pathway e.g. **chlorinated aliphatics**, some metals (e.g. Cr^{VI}) and nitroaromatics
- Removal rates and longevity are reductant dependent
  - **Relatively fast removal possible with strong reductants**
  - Extended contaminant contact to negate rebound and treat DNAPL (through better selectivity or longevity)



Reductants

- Variety of reductants
  - – From intrinsic biogeochemical processes with weaker reductants to engineered strong reductants
- Weaker reductants
  - – Fe^{II}-species
    - Oxides like green rust or magnetite
    - Sulfides like mackinawite or pyrite
- Stronger reductants
  - – Zero valent metals (e.g. ZVI)
    - ”Modified” ZVI (bimetallic, sulfidated)



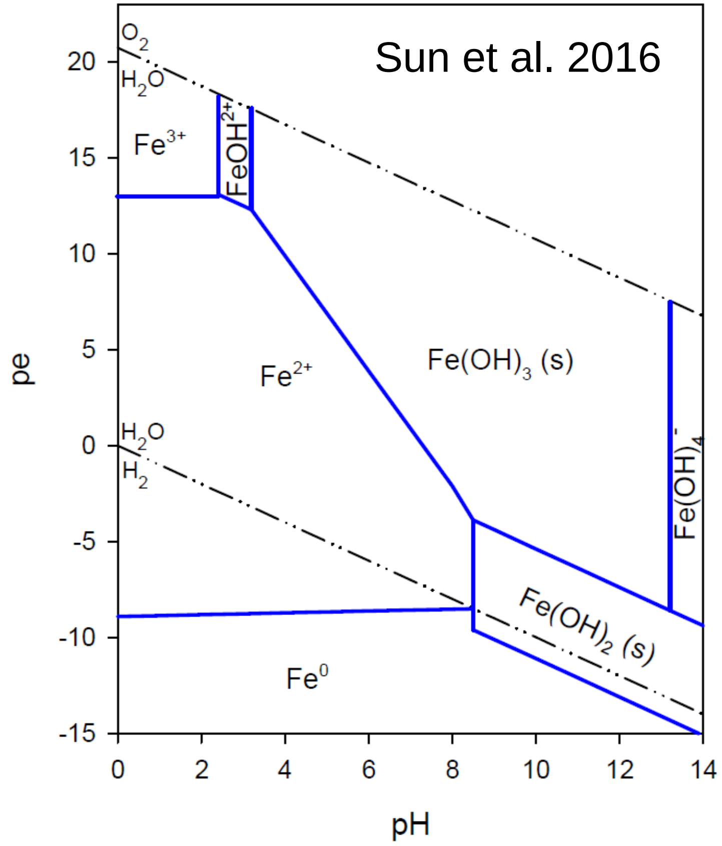
Tratnyek et al. 2014

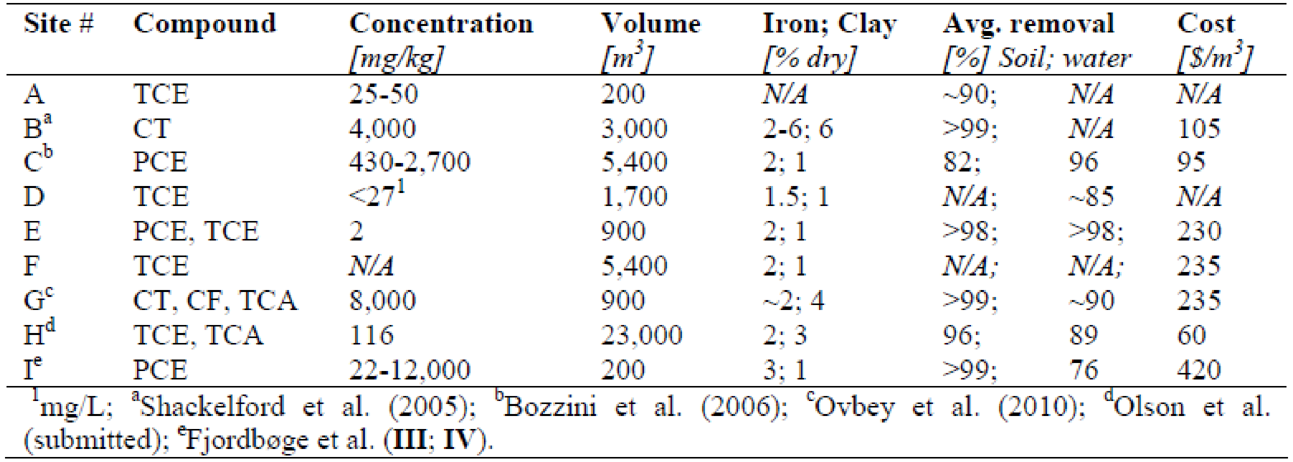
ZVI species

- Electron transfer to the contaminant

  $Fe^0 \rightarrow Fe^{2+} + 2e^-$

- Utilized with various particle sizes (nZVI, mZVI, gZVI) of different longevity
- Catalyzed bimetallic particles (noble metal catalyst like Pd) for more rapid reduction
- Sulfidated ZVI for better selectivity (less wasted on reaction with water)
- ZVI (mZVI/gZVI) is a field tested method with soil mixing (2-step)
  - **High pH raises an issue for a 1-step approach**


Sun et al. 2016



Site #	Compound	Concentration *[mg/kg]*	Volume *[m^3]*	Iron; Clay *[% dry]*	Avg. removal *[%] Soil; water*		Cost *[$/$m^3$]*
A	TCE	25-50	200	*N/A*	~90;	*N/A*	*N/A*
B[a]	CT	4,000	3,000	2-6; 6	>99;	*N/A*	105
C[b]	PCE	430-2,700	5,400	2; 1	82;	96	95
D	TCE	<27[1]	1,700	1.5; 1	*N/A*;	~85	*N/A*
E	PCE, TCE	2	900	2; 1	>98;	>98;	230
F	TCE	*N/A*	5,400	2; 1	*N/A*;	*N/A*;	235
G[c]	CT, CF, TCA	8,000	900	~2; 4	>99;	~90	235
H[d]	TCE, TCA	116	23,000	2; 3	96;	89	60
I[e]	PCE	22-12,000	200	3; 1	>99;	76	420

[1] mg/L; [a] Shackelford et al. (2005); [b] Bozzini et al. (2006); [c] Ovbey et al. (2010); [d] Olson et al. (submitted); [e] Fjordbøge et al. (**III**; **IV**).

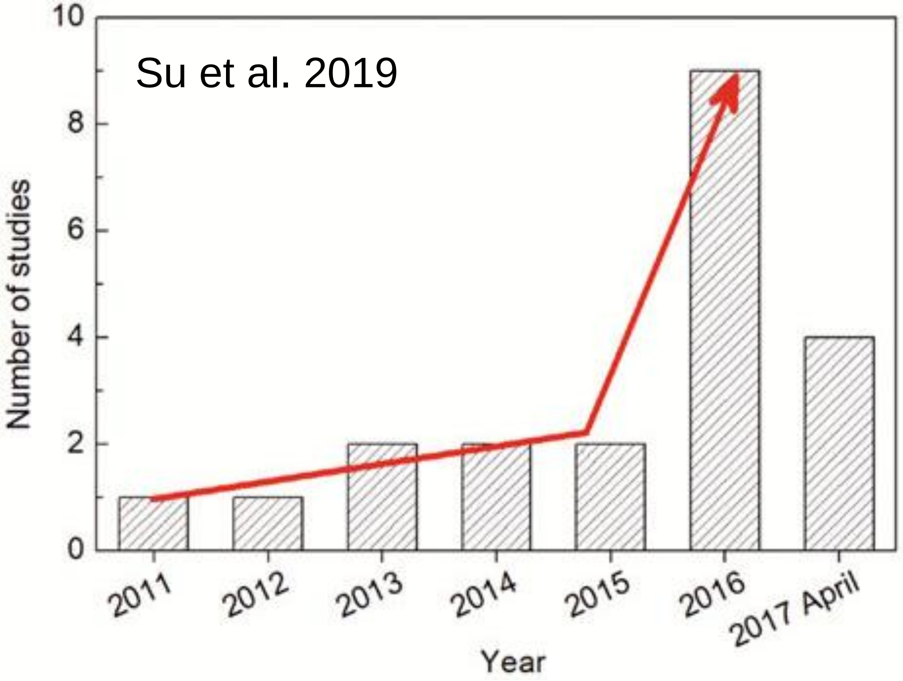
Sulfidated ZVI (and cement?)

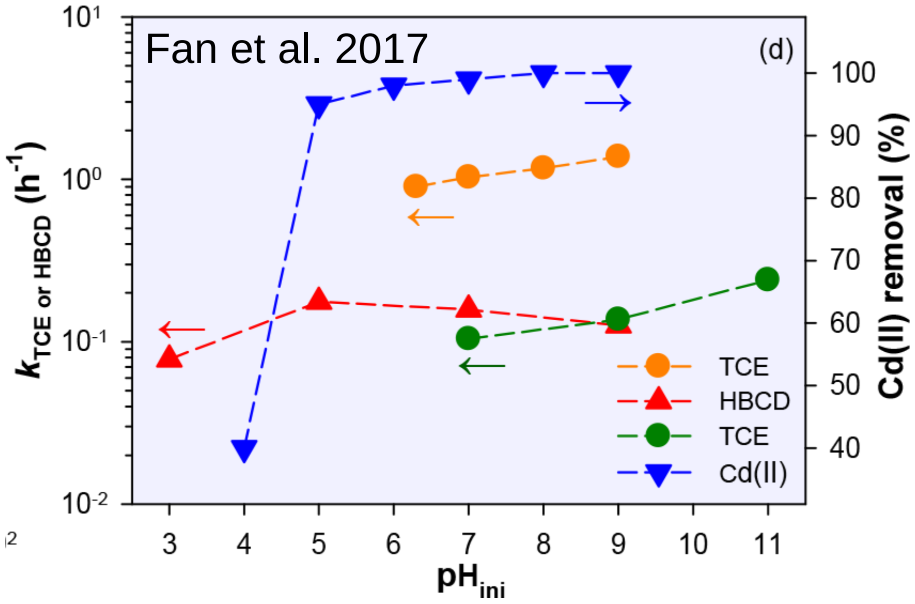
- Sulfidated ZVI is an upcoming product
  - – The sulfidated shell protects the ZVI core, which results in better selectivity
  - – Degradation seen under **alkaline** conditions (S-nZVI), where no degradation was seen with regular nZVI

- New method, so the mechanisms are not yet well described
  - – The optimal Fe/S ratio may depends on the target contaminant
  - – Only recently commercial available products

- Selectivity, pH resilience and strong reductant

  → Promising candidate for a 1-step approach with cement addition

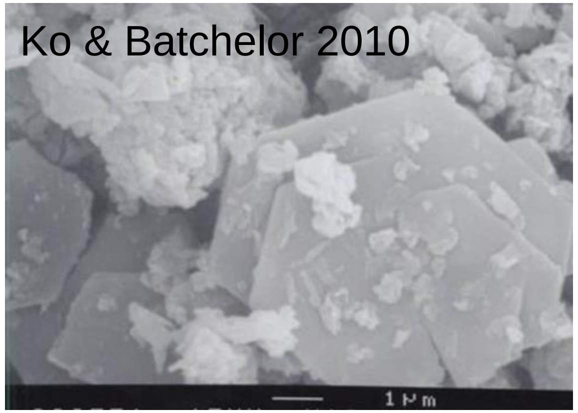


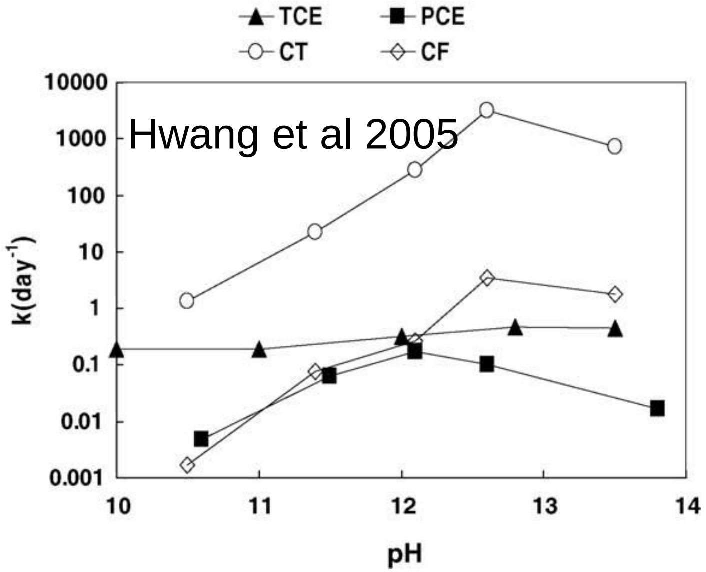


Fe^{II} minerals and salts (and cement?)

- Diverse group and varying reactivity found in laboratory studies; but it is generally found that:
  - – less reactive than ZVI
  - – sulfides are more reactive than oxides
  - – **the reactivity increase with increasing pH**
  - – the reactivity increase in the presence of dissolved Fe^{II}
    - Reactivity of Fe^{II}oxides on their own has been questioned

- Dissolved Fe^{II} alone is not a good reductant
- Lab experiments show degradation of chlorinated aliphatics with Fe^{II} in combination with cement
  - – Mechanism uncertain (Fe^{II} bound to CaO/cement surfaces)
  - – High pH (12-13) seems optimal for the degradation
  - → Promising candidate for a 1-step approach with cement addition


Ko & Batchelor 2010


Hwang et al 2005

In situ chemical oxidation (ISCO)

- Degradation by electron transfer from the contaminant to the oxidant

- Cover a broad range of contaminants e.g. CVOC, BTEX, PAHs, pesticides (versatility)
  - Mineralization of the contaminant to harmless products (e.g. CO_2, H_2O, ions)
  - Complex with several degradation pathways (risk of unknown intermediates, but normally few)

- Aggressive technology with **rapid** oxidant decomposition
  - Fast removal
  - Risk of rebound
  - DNAPL dissolution

Oxidants

Oxidant	Form	Potential (V) (acidic)	Potential (V) (alkaline)
Activated hydrogen peroxide (Hydroxyl radical)	$OH\bullet$	2.7	1.6
Activated persulfate (Sulfate radical)	$SO_4\bullet^-$	2.6	
Persulfate	$S_2O_8^{2-}$	2.0	
Hydrogen peroxide	H_2O_2	1.8	0.9
Permanganate	MnO_4^-	1.7	0.6

- Radicals are the strongest oxidants
  - Fast decomposition
  - Radical scavengers in form of common anions (e.g. NO_3^-, Cl^-, HCO_3^- , CO_3^{2-})

- Potential dependent on pH

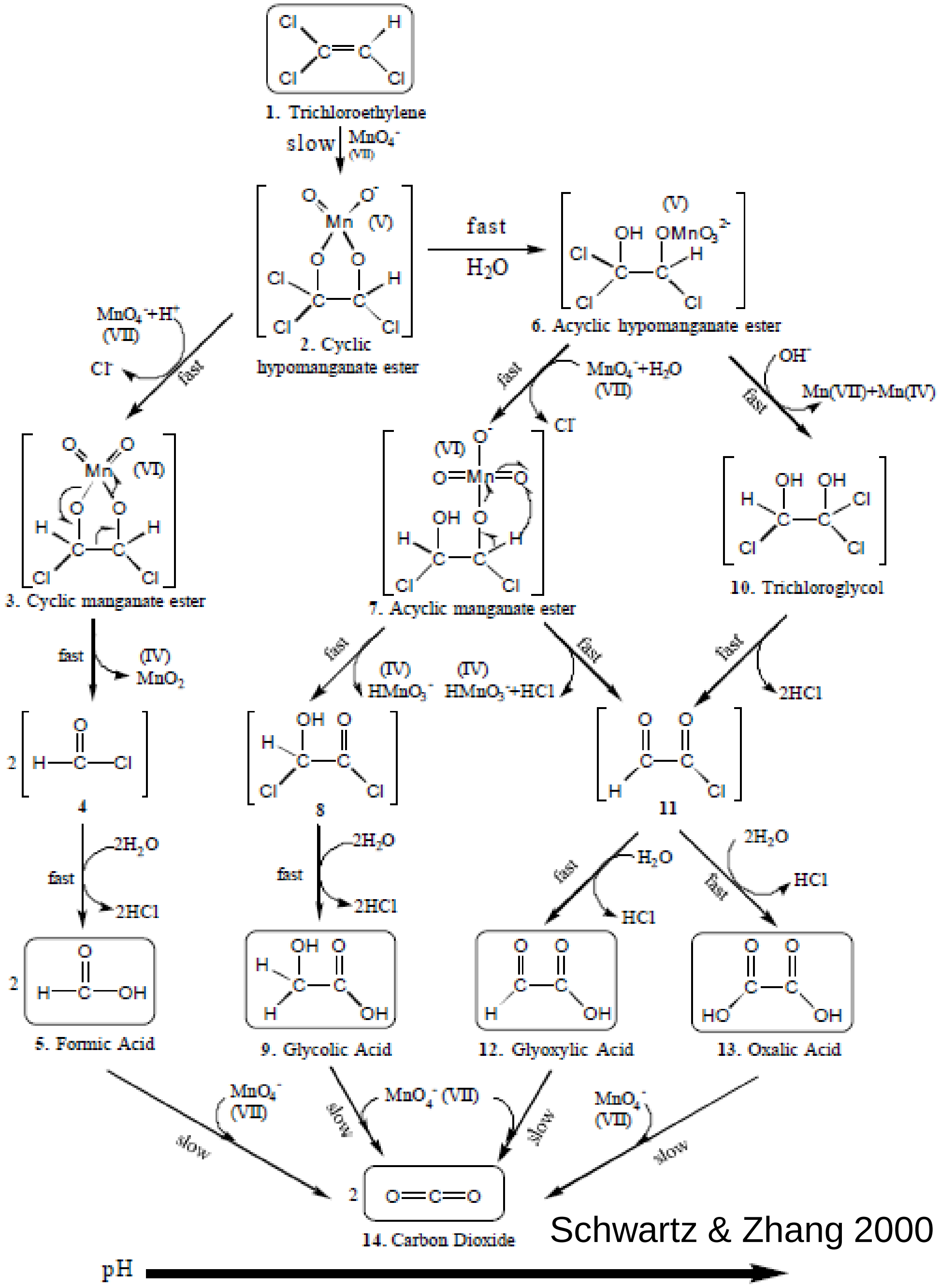
Permanganate

- Electron transfer from the contaminant

  $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

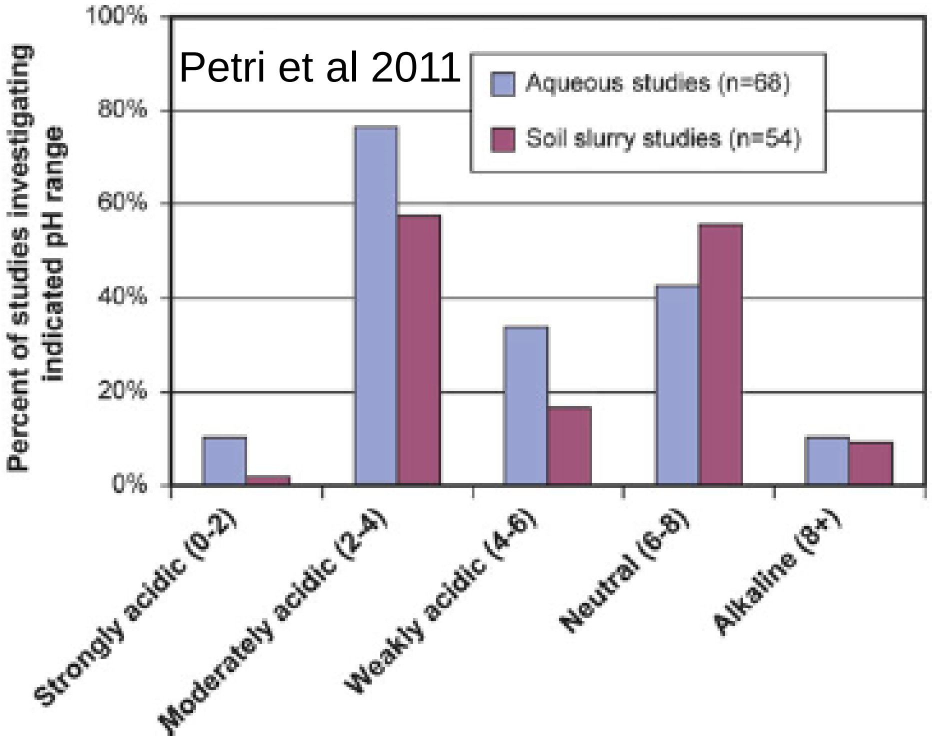
- Natural oxidant demand (NOD) can be significant (exceed OD of contaminant) and must be considered

- Field tested method in combination with soil mixing
  - One of the weaker oxidants (slower degradation)
  - Generally done as 2-step approach with a couple of days for reaction before stabilization



Schwartz & Zhang 2000

Activated hydrogen peroxide



- Activation by Fe^{II} (Fenton's reaction)

  $H_2O_2 + Fe^{2+} \rightarrow \mathbf{OH^{\bullet}} + OH^- + Fe^{3+}$

  $\mathbf{OH^{\bullet}} + H_2O_2 \rightarrow \mathbf{HO_2^{\bullet}} + H_2O$

  $Fe^{3+} + \mathbf{HO_2^{\bullet}} \rightarrow Fe^{2+} + O_2 + H^+$
- Fenton's reaction is efficient in acidic conditions (pH 2-4) and **inefficient at alkaline conditions** (Fe^{III} precipitation)

- Alternative: natural iron minerals or soluble organic ligands (chelates) with iron catalyst
  - The specific radicals produced depend on the pH, catalyst and oxidant concentration

- Field tested (2-step), but not typically used for soil mixing (health and safety concerns, vapor generation, very fast decomposition)

Activated persulfate

- Activation by iron, heat or **alkaline** conditions

  $S_2O_8^{2-} + Fe^{2+} \rightarrow \mathbf{SO_4^{\bullet -}} + SO_4^{2-} + Fe^{3+}$ (Iron)

  $S_2O_8^{2-}$ + Heat (40-70°C) $\rightarrow 2\mathbf{SO_4^{\bullet -}}$ (Heat)

  $S_2O_8^{2-}$ + pH (>10.5) $\rightarrow \mathbf{SO_4^{\bullet -}} + SO_4^{2-}$ (Alkaline)
- The quantity of radicals is dependent on the method of activation

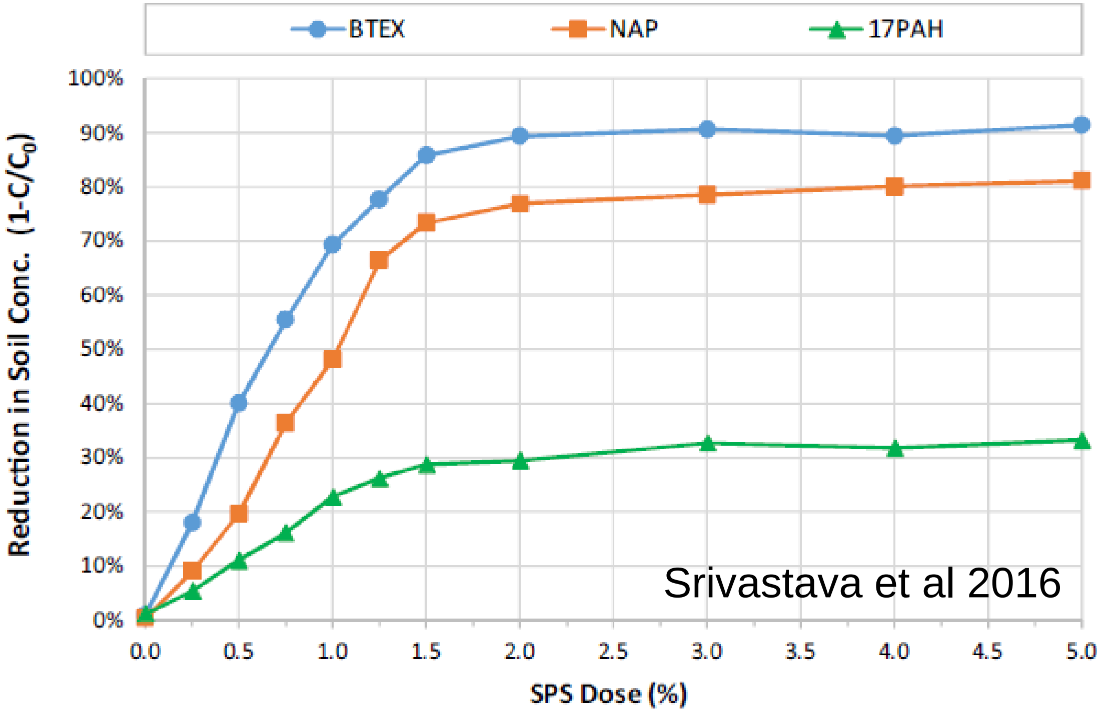
- Utilizes radicals, so **fast** decomposition
  - Radical scavenging **pH dependent** (e.g. CO_3^{2-} more potent scavenger than HCO_3^{-})

- Among the newer oxidants, so less studied

- Field tested with soil mixing and mainly lime addition for alkaline activation

Activated persulfate and cement

- Activation of persulfate under alkaline conditions (and elevated heat)
  → Promising candidate for a 1-step approach with cement addition



Srivastava et al 2016

Summary

Have:

- Methods that work with a 2-step approach: (1) degradation; (2) soil strength
  - A great variety of contaminants can be degraded by redox processes
  - Both ISCR and ISCO are field tested with soil mixing and can be applied
    - The preferable reactant will dependent on a number of factors e.g. the type of contaminant, the timeframe, and the specific clean-up criteria

Want:

- Methods that work with a 1-step approach
  - Ongoing development
  - Interactions with cement hydration/curing processes are complicated
  - Promising candidates for both ISCR and ISCO

Thank you for your attention