Practical Applications for Nanoremediation

Session 1

RemTech, Ferrara Exhibition Center, Ferrara, Italy

21 September 2016

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Agenda for Session 1

Time (Hrs)	Title	Presenter
0930 - 1030	A Primer on Nanoremediation – History, Applications, and Issues	D.W. Elliott
1030 - 1045	Break	
1045 - 1145	Nanoremediation in the EU - Impacts of NanoRem and Technology Combinations	M. Cernik
1145 - 1200	Break	
1200 - 1300	Key Field Applications of Nanoremediation – Lessons Learned and Future Directions	P. Kvapil

Introduction of Speakers

- Daniel W. Elliott, Ph.D. – Geosyntec Consultants, USA

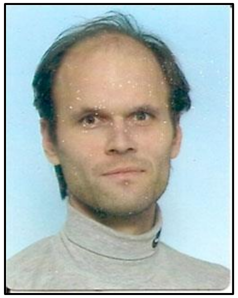
“Primer on Nanoremediation – History, Applications, and Issues”

- Miroslav Cernik, Ph.D. – Technical University of Liberec, Czech Republic

“Nanoremediation in the EU – Impacts from NanoRem and Technology Combinations”

- Petr Kvapil, Ph.D. – Aquatest a.s., Czech Republic

“Key Field Applications of Nanoremediation – Lessons Learned and Future Directions”



Primer on Nanoremediation – History, Applications, and Issues

Daniel W. Elliott, Ph.D., Senior Consultant

Ewing, New Jersey, U.S.A.

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Agenda

I. Why Nanoremediation?
II. Nanoscale zero-valent iron (nZVI) – origins, properties, and varieties
III. nZVI applications and chemistry
IV. Using nZVI in the field
V. nZVI data needs and future directions

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Section I

Why Nanoremediation?

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I. Challenging sites need powerful cleanup strategies

- Since the 1970s, hundreds of billions of $ have been spent to clean up contaminated sites in the U.S.[1]
- Scale of the problem (U.S.):
  - NAS (2012)[1]: >126,000 contaminated sites remain with a cost-to-cure of $110-127 billion USD
  - EPA (2004): >300,000 sites requiring remediation through 2033 at a cost exceeding $200 billion USD
- ~10% have "complex" hydrogeology and/or chemistry[1]:
  - Low permeability zones, deep aquifers, fractured bedrock, matrix diffusion, etc.
  - Recalcitrant contaminants, DNAPL, incompatible geochemistry, etc.
- Nanoremediation is a promising remedial option

1. Cavanaugh et al. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. 2012. National Academy of Sciences

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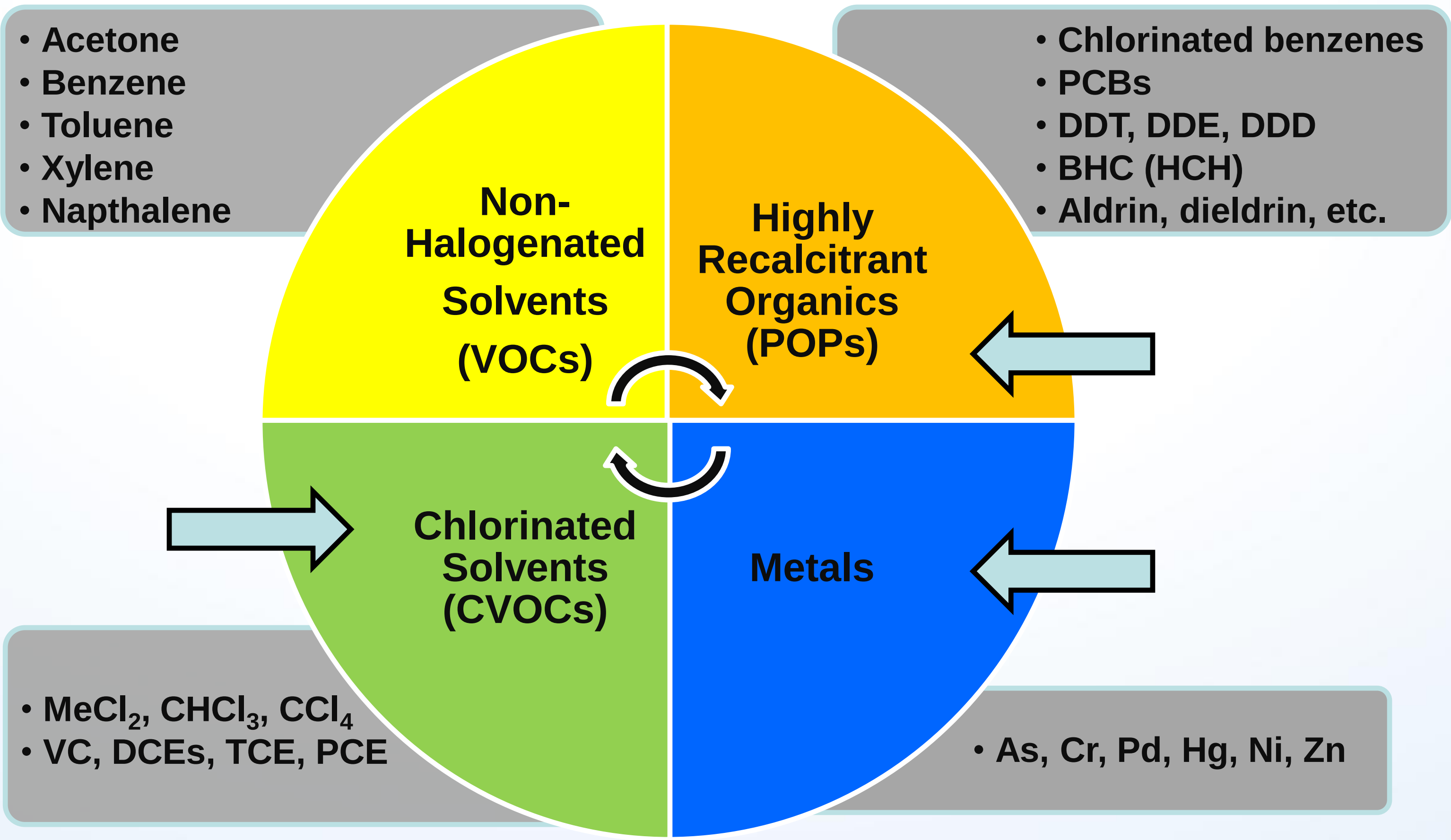
I. Contaminant candidates for nanoremediation



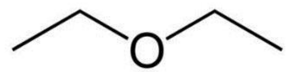
Others: MTBE, ClO_4^-, PFC

I. The challenge of recalcitrance

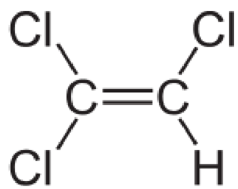
Nanoremediation Approaches:

- Oxidative vs. reductive
- Abiotic vs. biotic

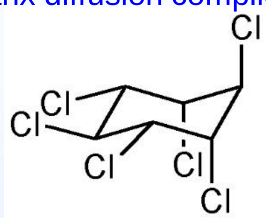
Slowly transformed



Ethyl ether
Aqueous soluble; Resistant etheric linkage

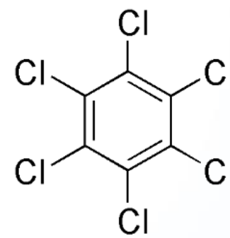


cVOCs (PCE, CT & 1,1,1-TCA)
Moderate aqueous solubility; Multiple degradation options but form DNAPLs & matrix diffusion complications

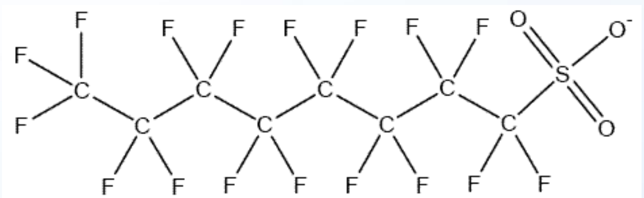


Lindane (γ-HCH)
Low aqueous solubility; Multiple slow to moderate remedial options

Persistent



Hexachlorobenzene
Very slow anaerobic biodegradation; Limited remedial options



PFC
Very resistant to degradation; Limited remedial options

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I. Attacking remedial timeframes and spend

- Traditional remedial methods often involve long timeframes and significant spend
  - Especially early generation P&T
- Existing *in situ* approaches can have major technical challenges
  - Contaminant rebound, matrix diffusion, degradation-related intermediates, etc.
- Nanoremediation offers the potential for:
  - Faster transformation kinetics
  - Extending the spectrum of degradable contaminants
  - Portable, targetable (smart) delivery to impacted areas
  - Better penetration of impacted matrices

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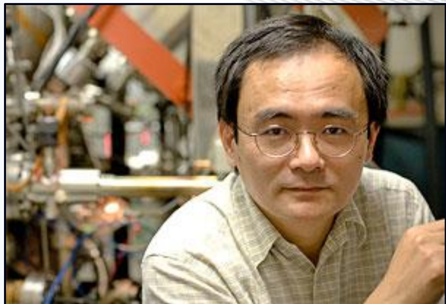
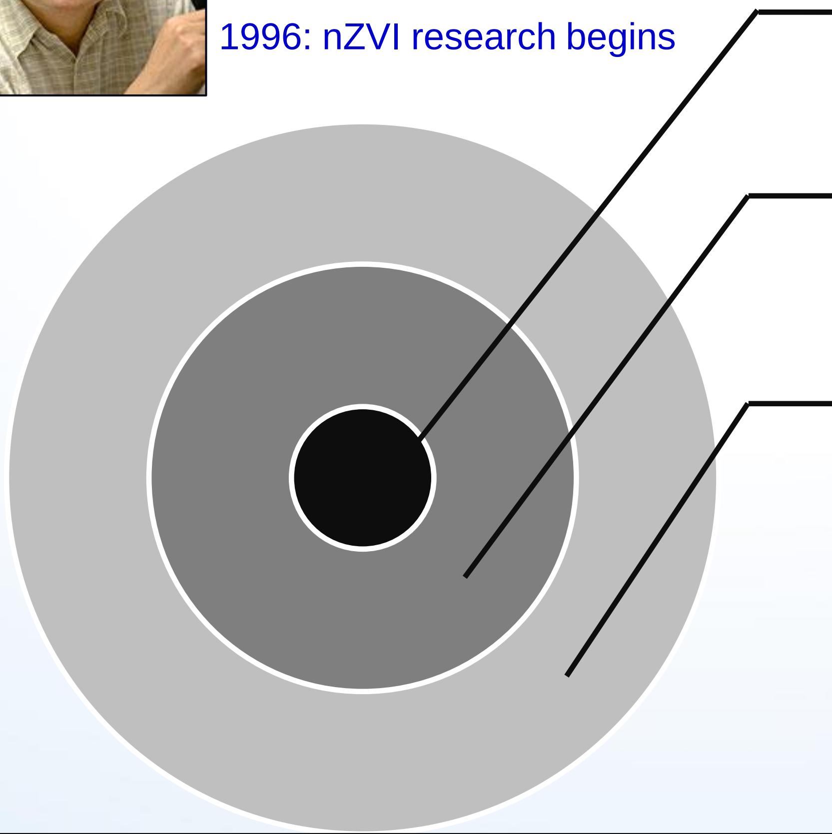
Section II

nZVI – origins, properties, and varieties

II. Nanoremediation roots in ZVI

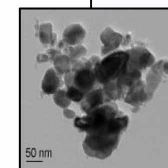


1996: nZVI research begins



Nanoscale, nZVI (<100 nm)

Application: In-situ inj. for source area & dissolved plume



Microscale, mZVI (1-100 μm)

Application: Backfill, some in-situ inj.

Granular, gZVI (mm)

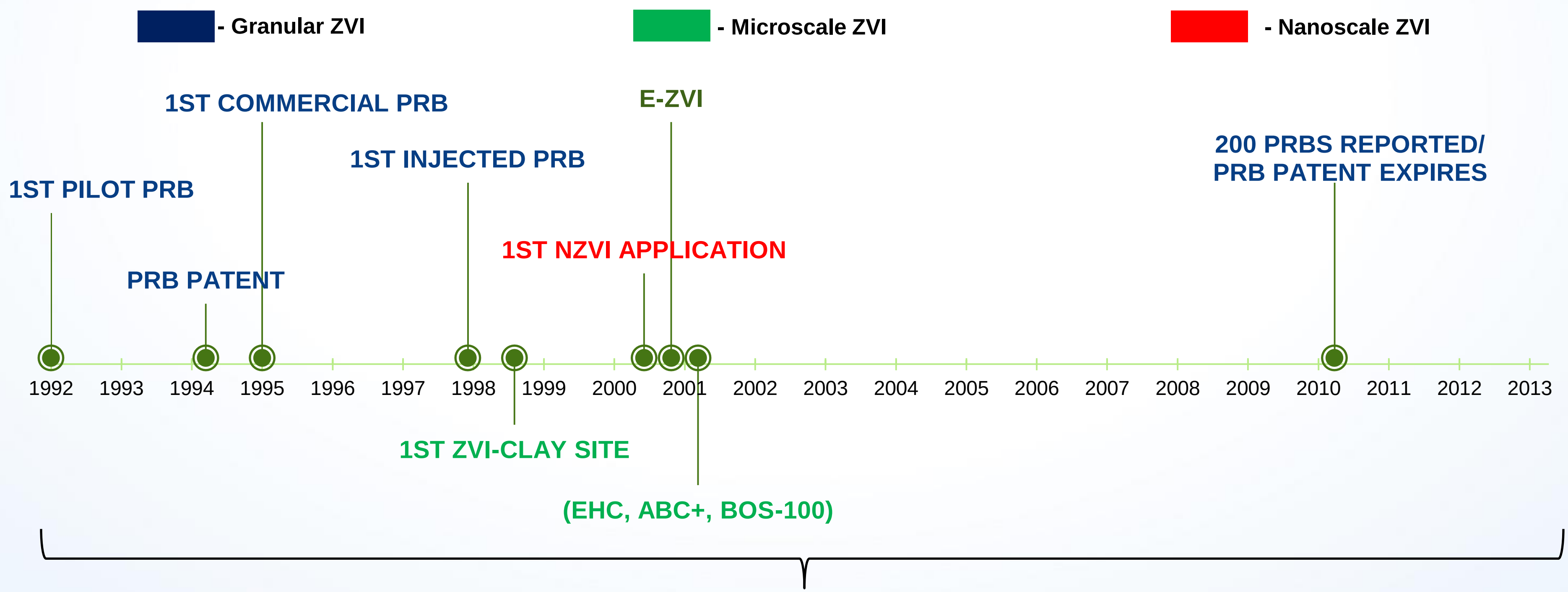
Application: PRBs, backfill, etc.

Reactivity

gZVI → mZVI → nZVI

Specific surface area, m^2/g

II. Timeline of ZVI utilization in remediation



- Use of ZVI in remediation evolved from U. of Waterloo research in late 1980s
- Significant research and applications interest: >1,400 papers & reports
- mZVI being increasingly used in- and ex-situ since the late 1990s
- nZVI occupies a niche role in the US, growing in parts of the EU

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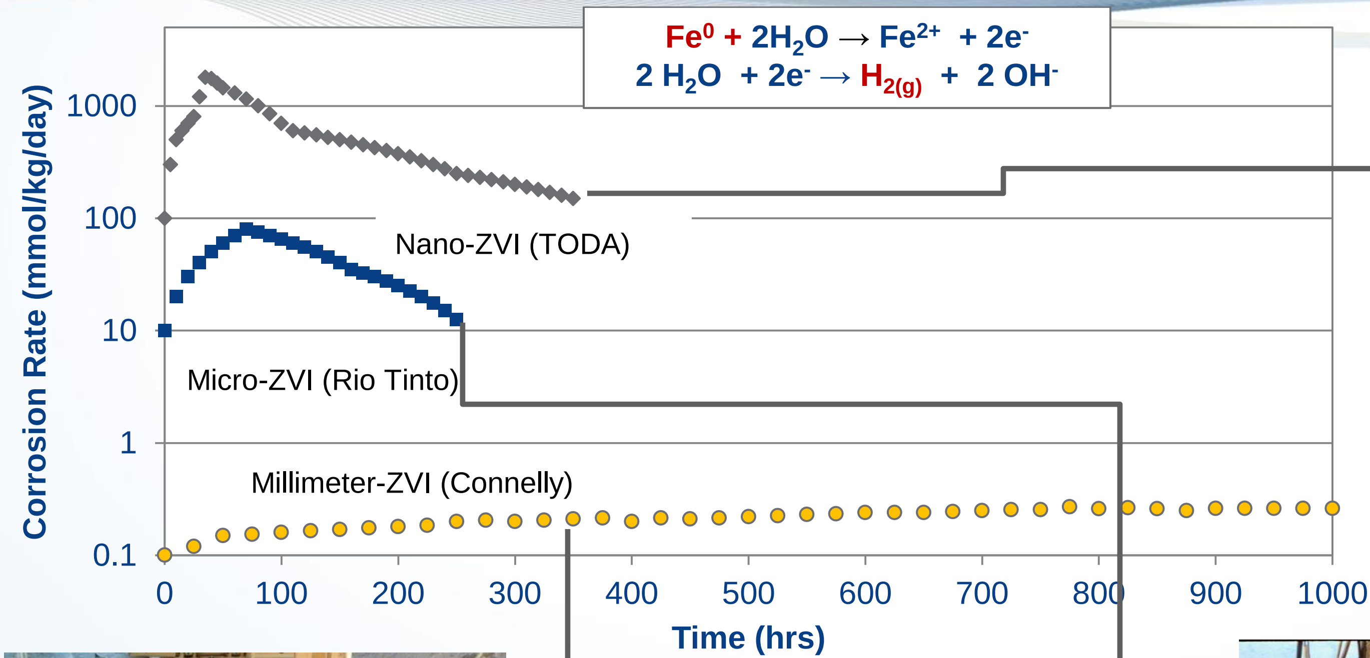
II. ZVI – size does in fact matter

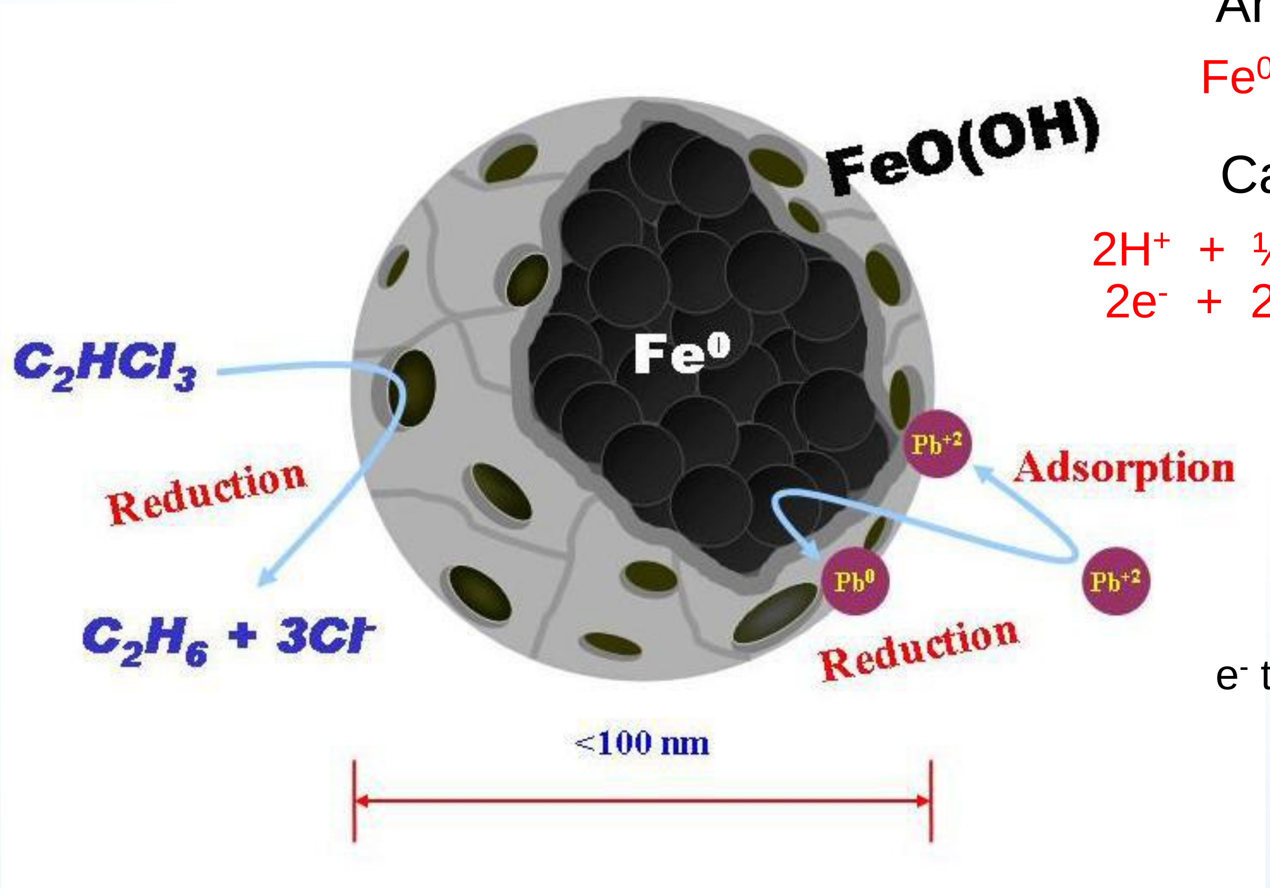


nZVI: Source zone or hot spot treatment, injection through wells or direct injection.

gZVI: PRBs for plume migration control. Trenching and backfill. SZ-Soil mixing (ZVI-clay).

mZVI: Direct plume treatment. Injected PRBs. DPT or fracturing.

II. Conceptual model



Redox reactions

Anode

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

Cathode

$2H^+ + ½ O_2 + 2e^- \rightarrow H_2O$

$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$

Core-shell model

e^- transfer across oxide layer

- Contaminant degradation by nZVI is surface-mediated

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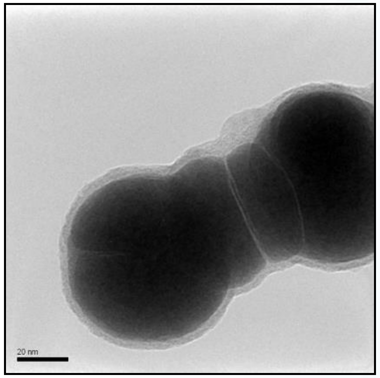
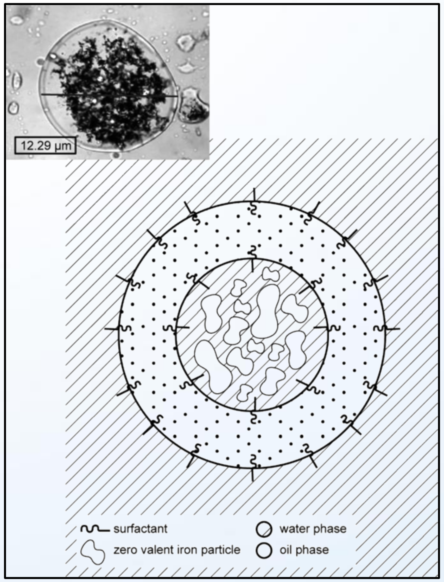
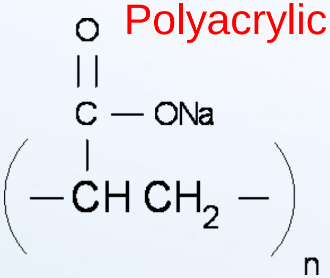
II. A plethora of iron nanoparticles

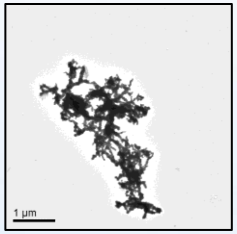
- Bare nZVI & nFe-oxides
- Bimetallics (Fe/Pd, etc.)
- Supported nZVI
  - Carbon or polymeric bead substrate
- Emulsified ZVI (eZVI)
  - nZVI or mZVI within emulsified oil micelles
- Surface-modified nZVI
  - Surfactant/polymeric surface architectures
    - Polyacrylic acid (PAA) stabilized (others = NaHMP, CMC)



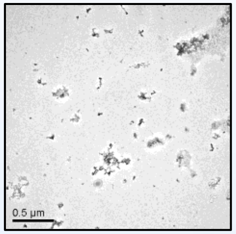




0% PAA

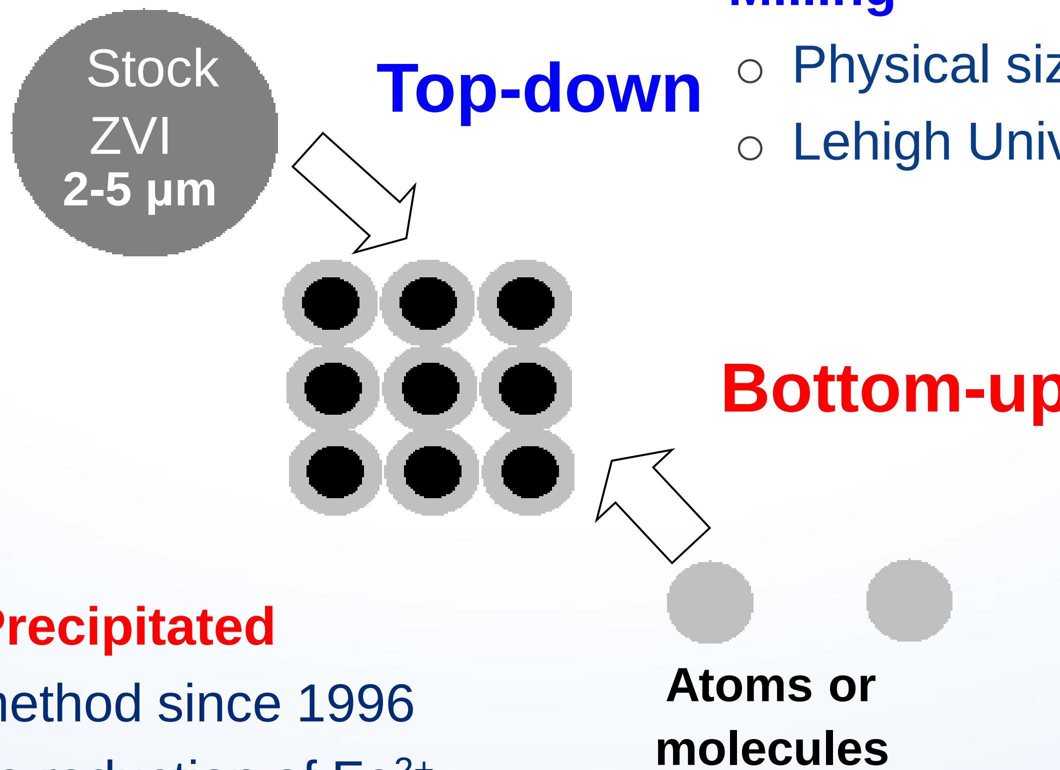


20% PAA



II. So how is this stuff made?

- **Mechanically Ground / Ball-Milling**
  - Physical size reduction
  - Lehigh University (2005)



- **Chemically Precipitated**
  - Classical method since 1996
  - Borohydride reduction of Fe^{2+} or Fe^{3+} salts

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II. Commercial sources of ZVI for remediation

- Hepure
- OnMaterials
- Connelly GPM
- BASF
- Rio Tinto
- NANO IRON, s.r.o.
- Adventus/PeroxyChem
- Bio Blend Technologies
- RemQuest*
- Reade*
- Gotthart Maier Metallpulver GmbH
- Peerless Metal Powders
- GeoNano Env. Tech.
- Höganäs
- Plus others…

- Granular ZVI (blue) - Microscale ZVI (green) - Nanoscale ZVI (red)

* - Principally research quantities

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II. How much does this stuff cost?

Scale	Size Range	SSA (m^2/g)	Cost[1] ($USD/kg)
Millimeter (gZVI)	0.1mm - 2mm	1 - 2	$0.70 - $1.65
Micrometer (mZVI)	20μm - 300μm 1μm - 20μm	3 - 5	$2.00 - $3.00 $4.50 - $22.00
Nanometer (nZVI)	50nm - 200nm	30 - 58	$55 - $170

SSA –specific surface area

1 – Cost can also be expressed as $USD/m^2 of surface (per 1,000 m^2 of surface):

gZVI = $0.35 - $1.65
mZVI = $0.40 - $7.33
nZVI = $0.95 - $5.67

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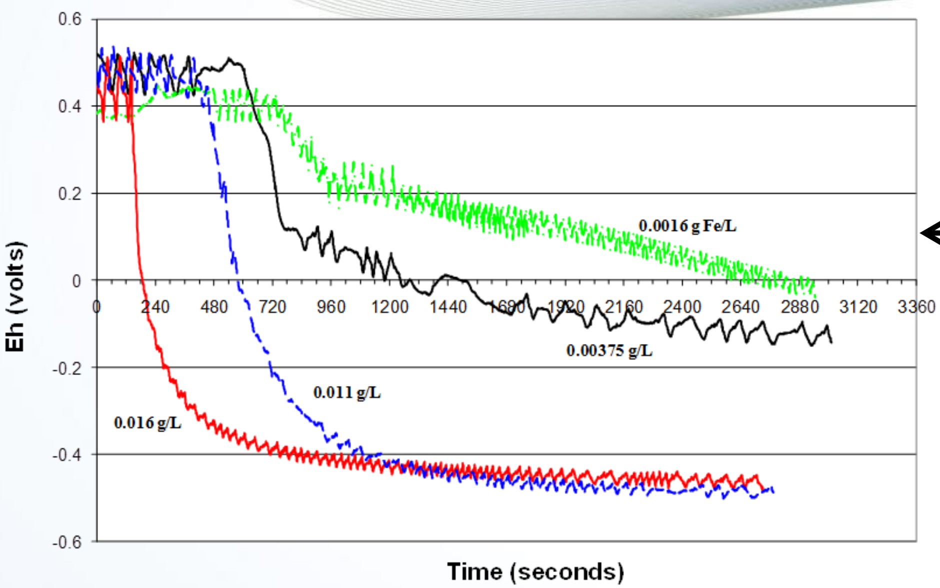
Section III

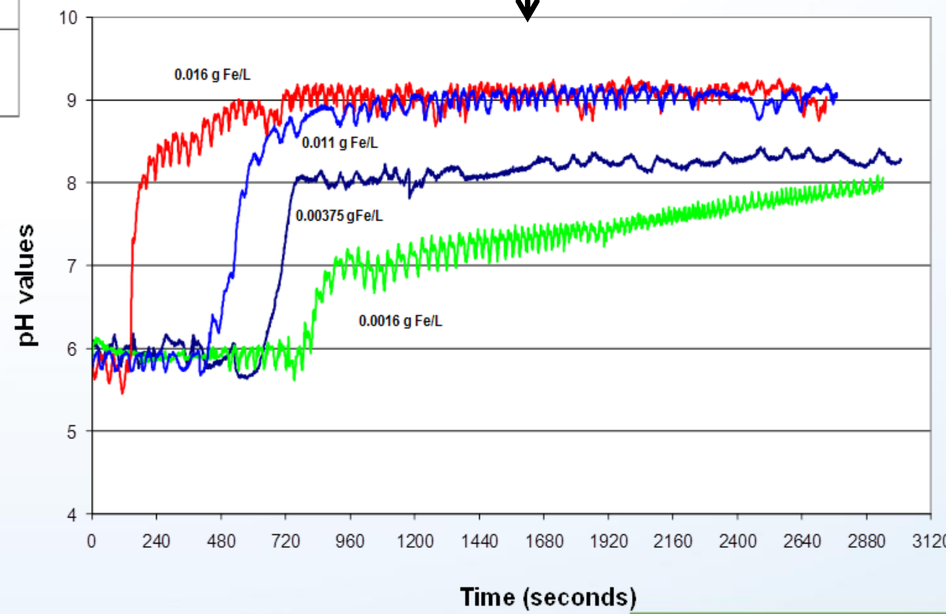
nZVI – applications and chemistry

III. Profound pH and ORP impacts

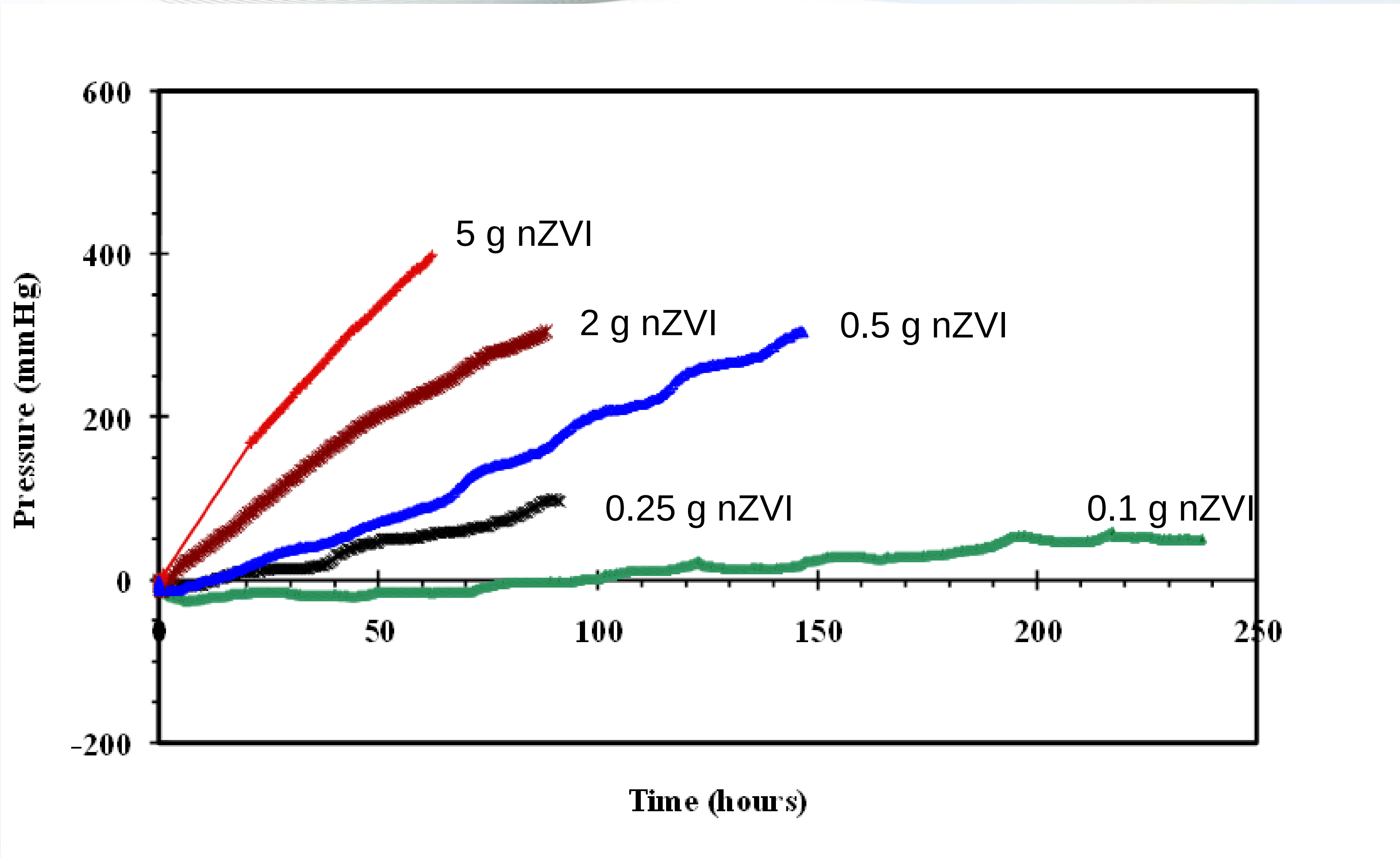


$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2e^-$

$2\,H_2O + 2e^- \rightarrow H_{2(g)} + 2\,OH^-$



III. Dynamic H_2 evolution



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III. Amenable contaminant classes

Ethenes
PCE
TCE
cis-1,2-DCE
trans-1,2-DCE
1,1-DCE
VC

Methanes*
PCM (CT)
TCM (CF)
TBM

Ethanes*
1,1,2,2-TeCA
1,1,1,2-TeCA
1,1,2-TCA
1,1,1-TCA
1,1-DCA
CFC-11
CFC-113
EDB

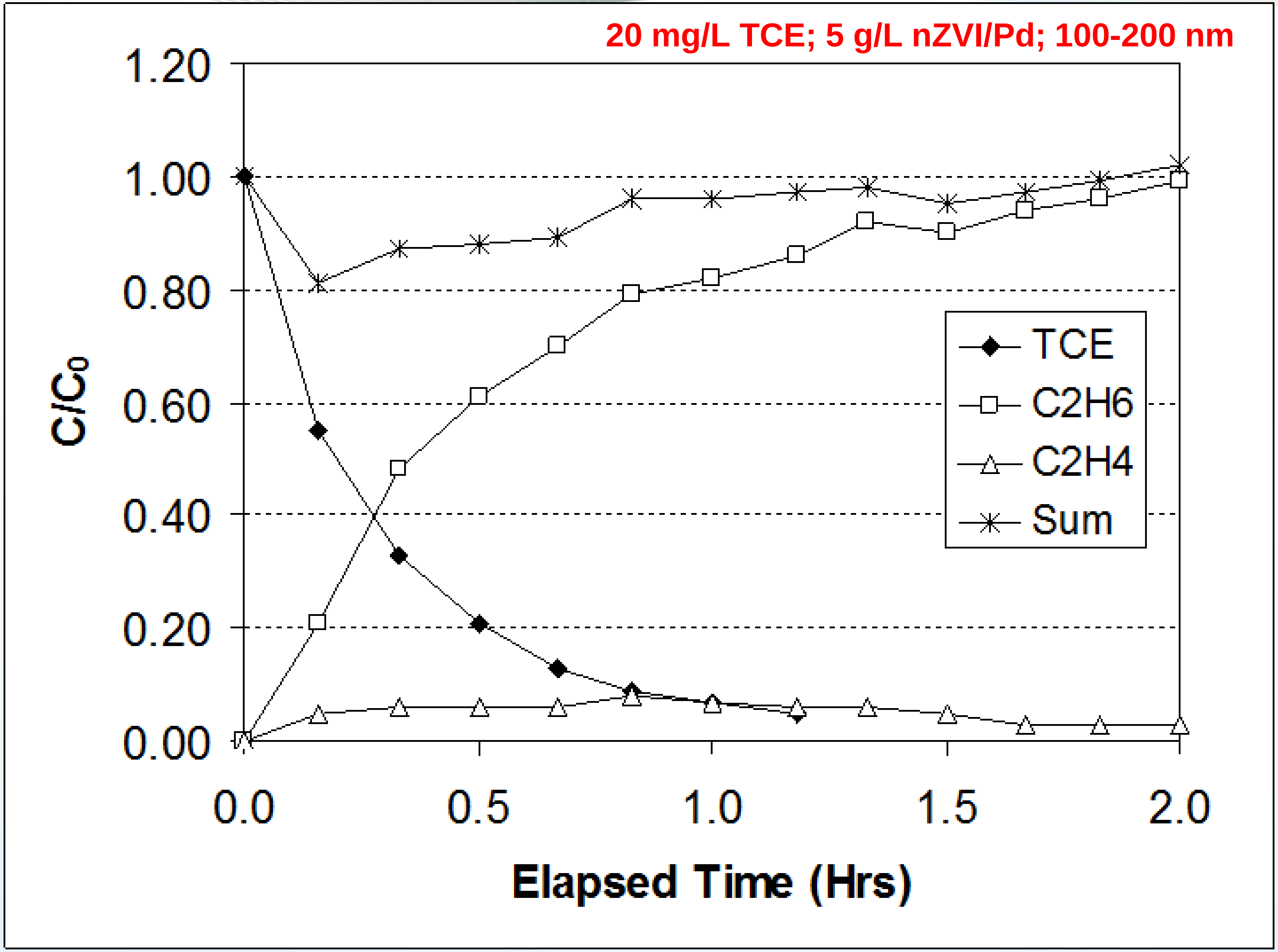
Others
Perchlorate
NDMA
Metals (Cr^{6+}, Hg^{2+}, $As^{3+,5+}$)

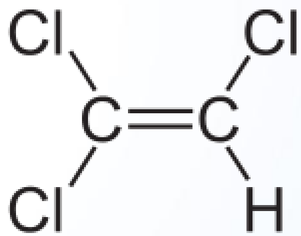
Propanes
1,2,3-TCP
1,2-DCP
DBCP

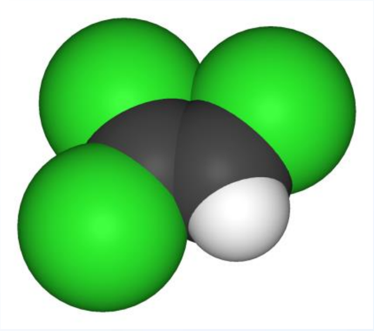
POPs
γ-HCH (BHC)
DDT
Chlorobenzenes
PCB

* 1,2-DCA, CA, DCM, CM difficult to treat by ZVI alone

III. Degradation of TCE by nZVI/Pd







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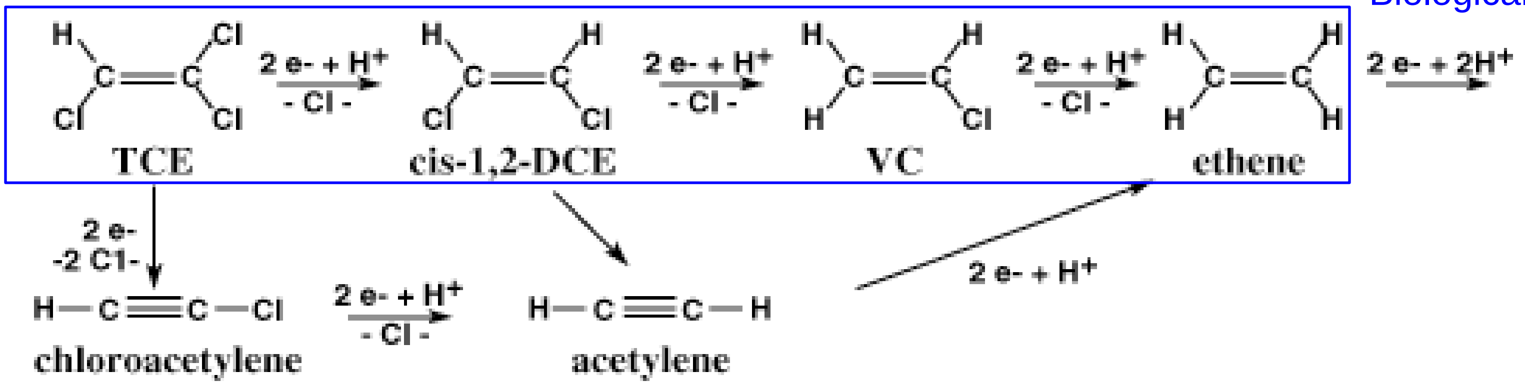
III. A tale of two degradation pathways

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$
$$C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^-$$

Hydrogenolysis: Minor Pathway

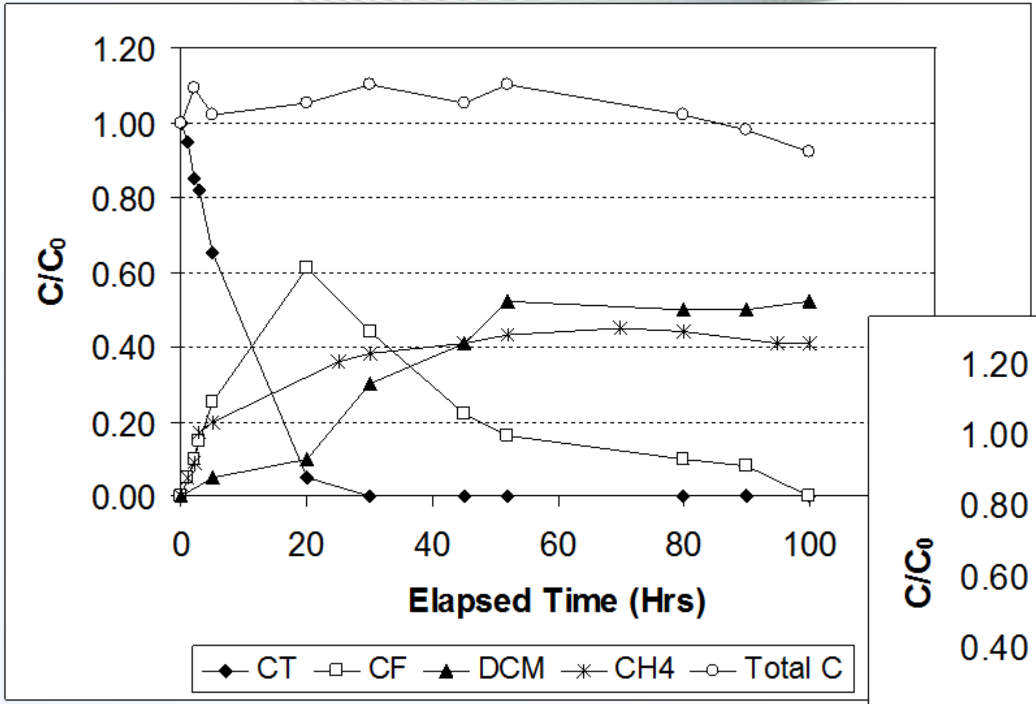
Biological route



ß–Elimination: Main Pathway

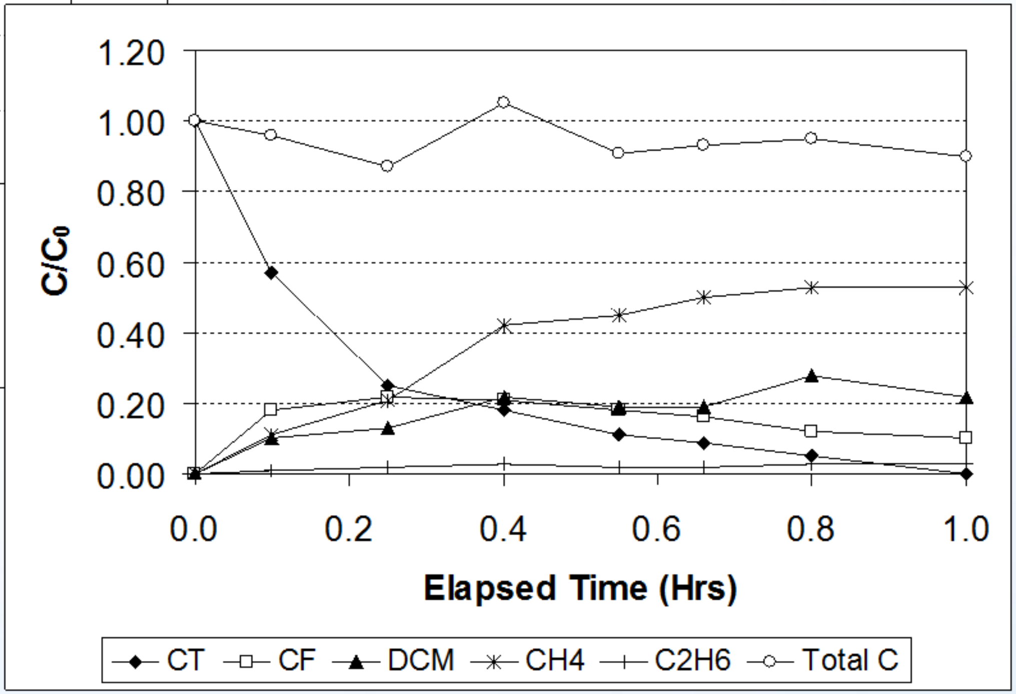
- First-order kinetics
- Requires direct contact with ZVI surface
- Can be difficult to discern abiotic and biotic degradation of TCE at the field-scale

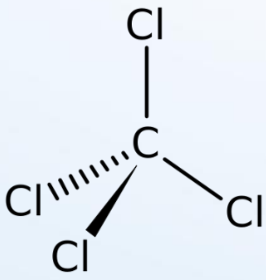
III. Degradation of CT

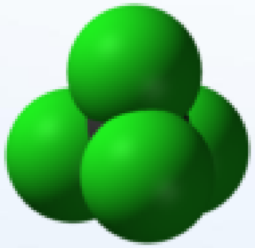


15.86 mg/L CT; 12.5 g/L nZVI; 100-200 nm

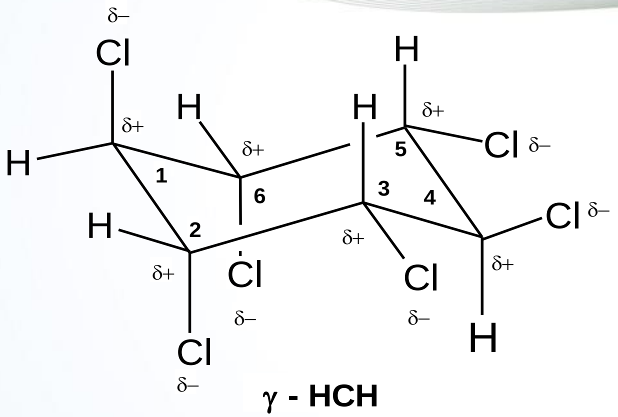
15.4 mg/L CT; 12.5 g/L nZVI/Pd; 100-200 nm







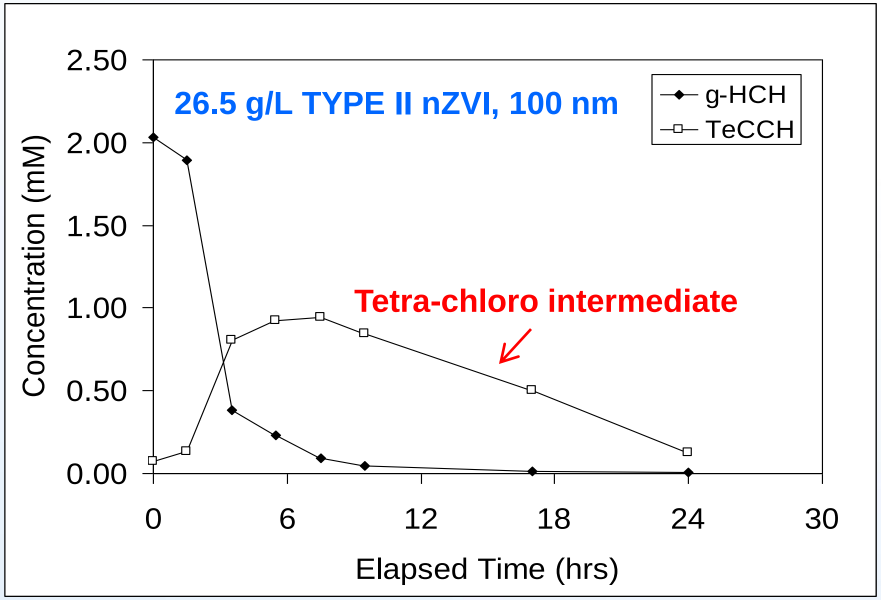
III. Degradation of γ-HCH

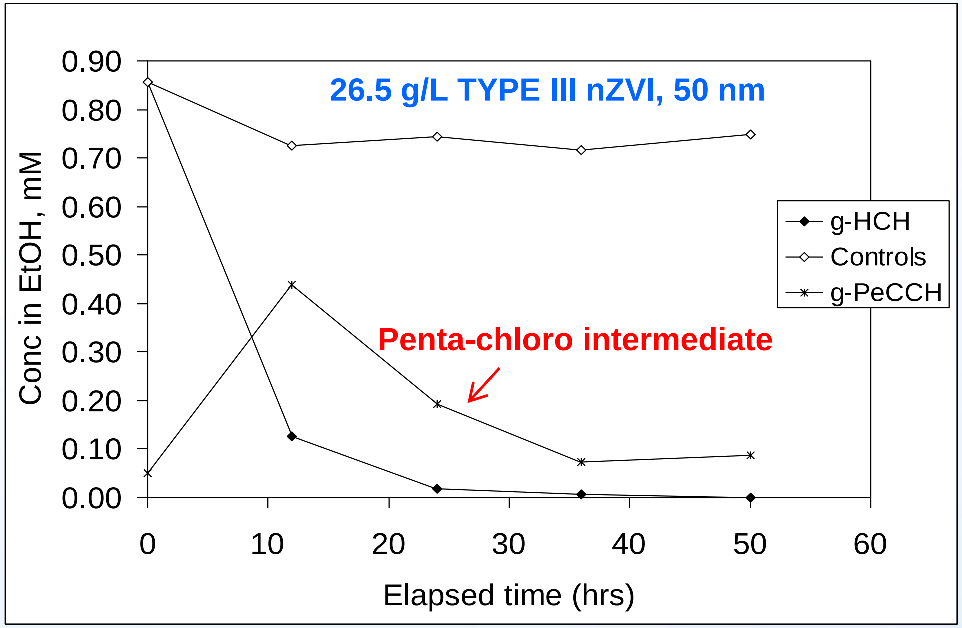


γ-HCH, BHC, "lindane" – a classic organochlorine pesticide

- 10MM metric tons used globally from 1940s into 1990s
- Recalcitrant, low aq. sol and high sorption potential

→ Major remediation challenge in soils, sediments, GW
→ Recalcitrant to bioremediation





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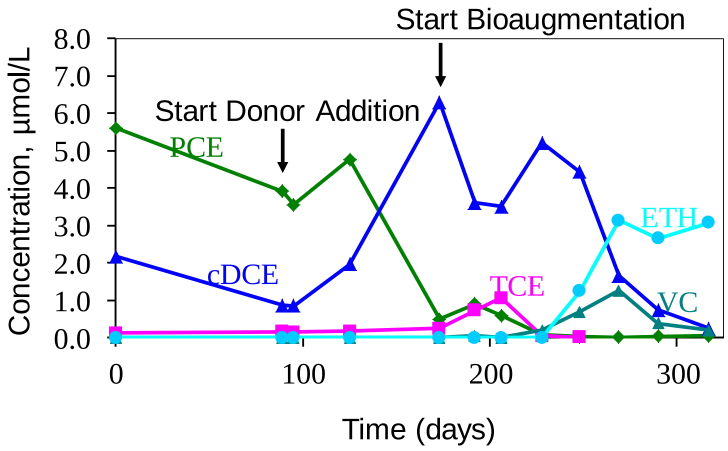
III. ZVI and EISB – perfect together

- Enhanced *in situ* biodegradation (EISB) of cVOCs is widely practiced in North America & EU
  - Dhc for chloroethenes
  - Dhb for chloromethanes & ethanes
- H_2 is the ultimate electron donor
- ZVI promotes:
  - Appropriate reducing pH/ORP profile
  - Reduction of H_2O yields H_2 and OH^-
- ZVI impacts to the microbial consortia are transient
  - Field evidence suggests that Dhc, Dhb population growth is often enhanced
- Strong synergies in coupling ZVI with EISB

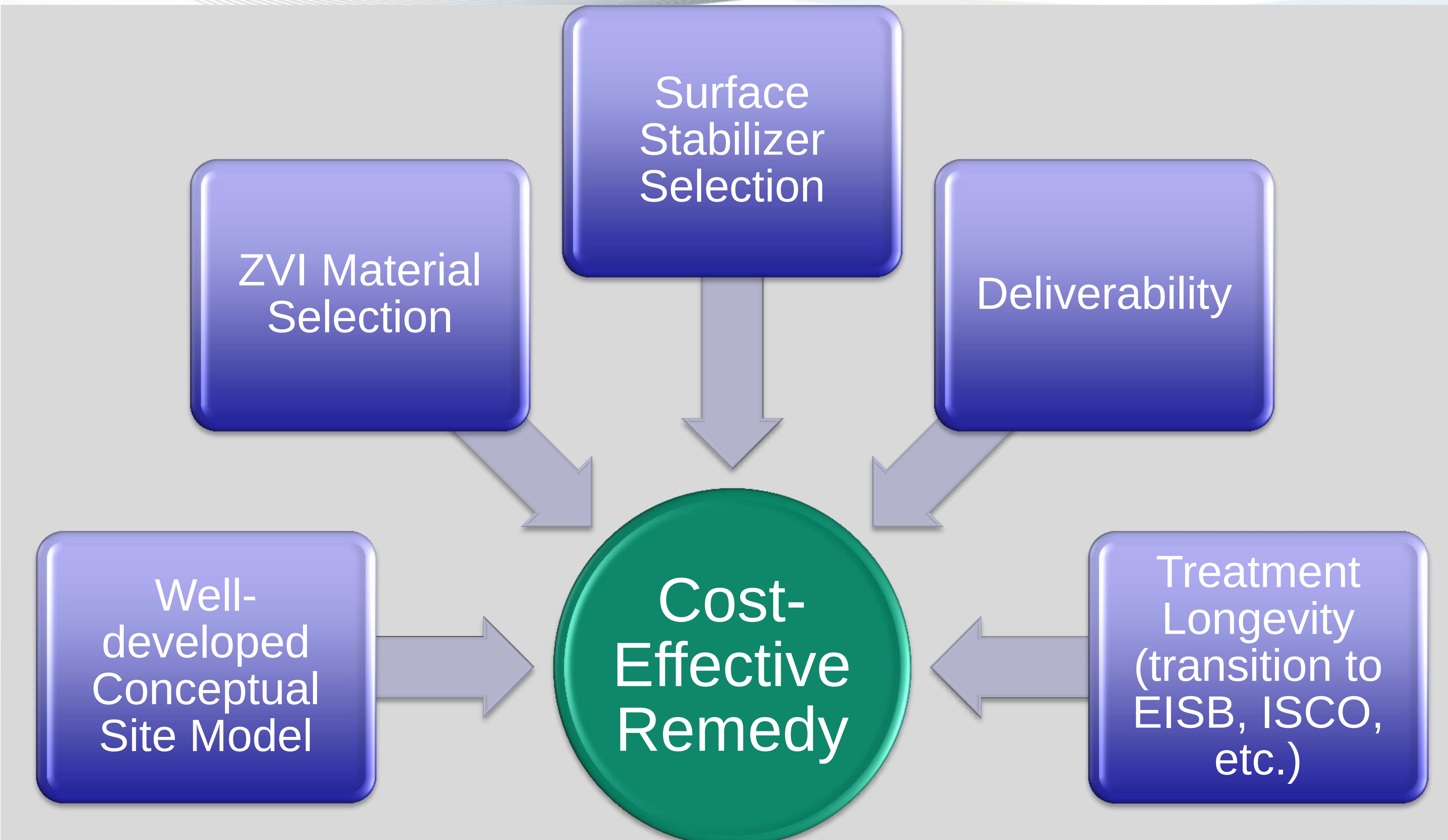
Results: Monitoring Well B1



Section IV

Using nZVI in the field

IV. Key considerations



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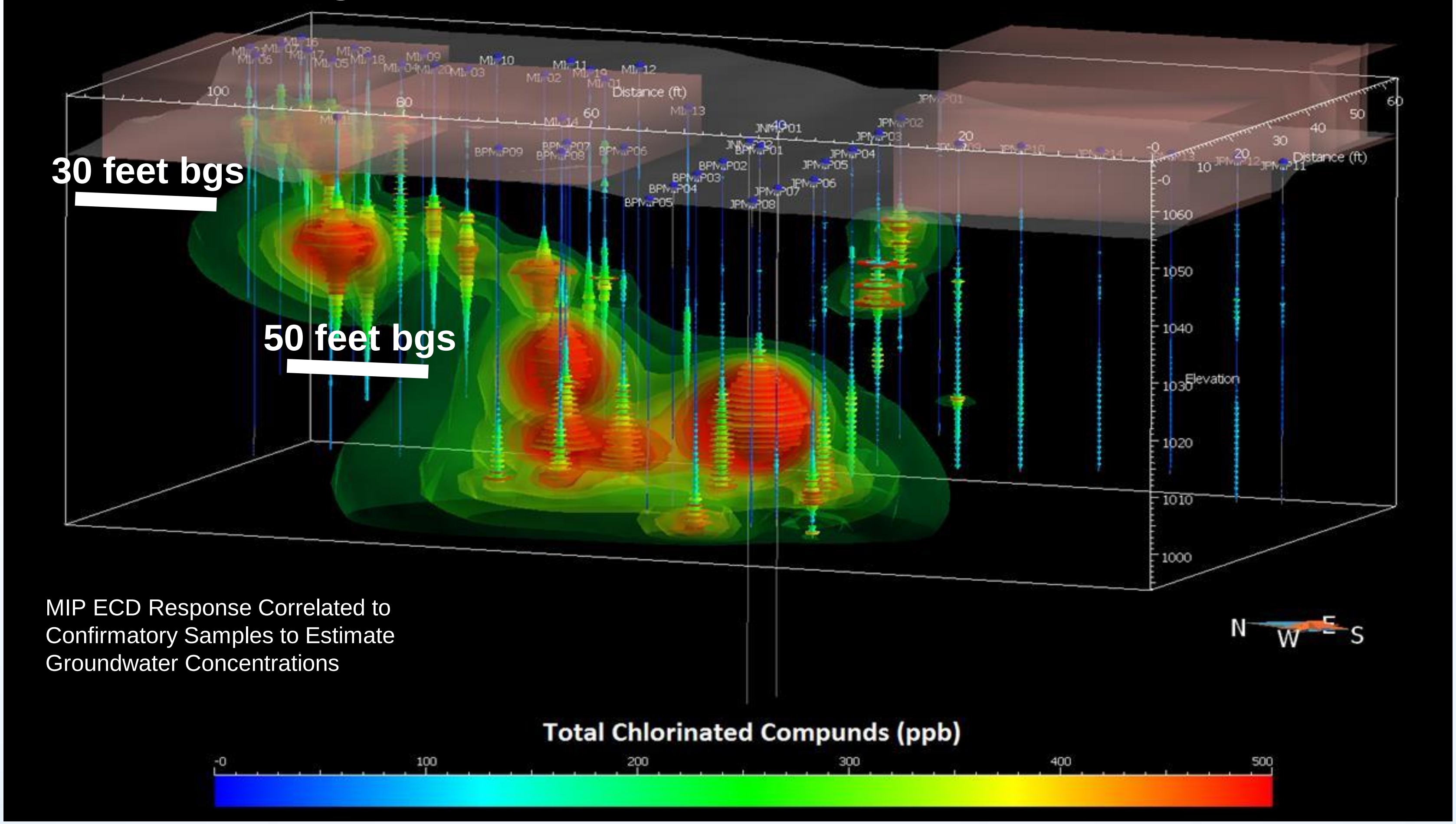
IV. Robust CSM is a must

View looking northeast



MIP ECD Response Correlated to Confirmatory Samples to Estimate Groundwater Concentrations

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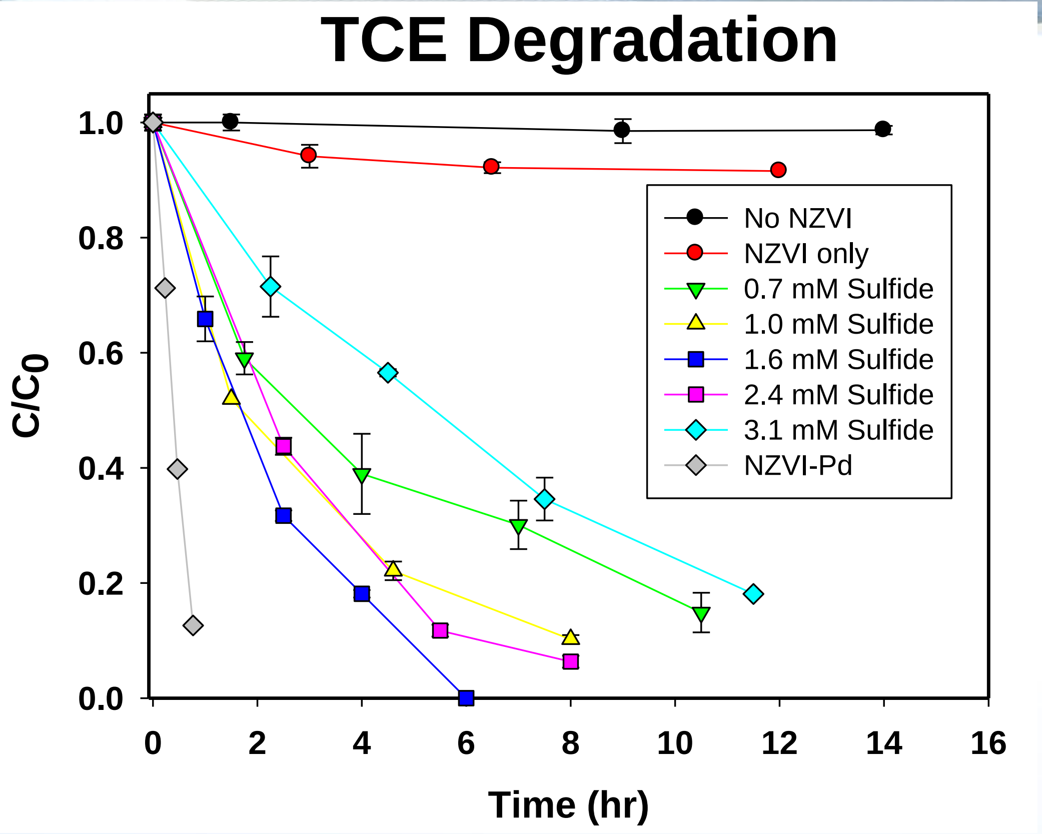
IV. Material selection considerations



Provided by Dr. M. Borda - Research conducted by McGill University Department of Civil Engineering

- What type of nZVI to use?
  - Size range, vendors, cost
- Source area vs. plume
- Must be integrated with SCM & delivery method
- Multiple injection campaigns likely needed
- New developments
  - Sulfate may form sulfide at ZVI surface
  - Sulfidized ZVI can dramatically improve cVOC reduction & selectivity using ZVI

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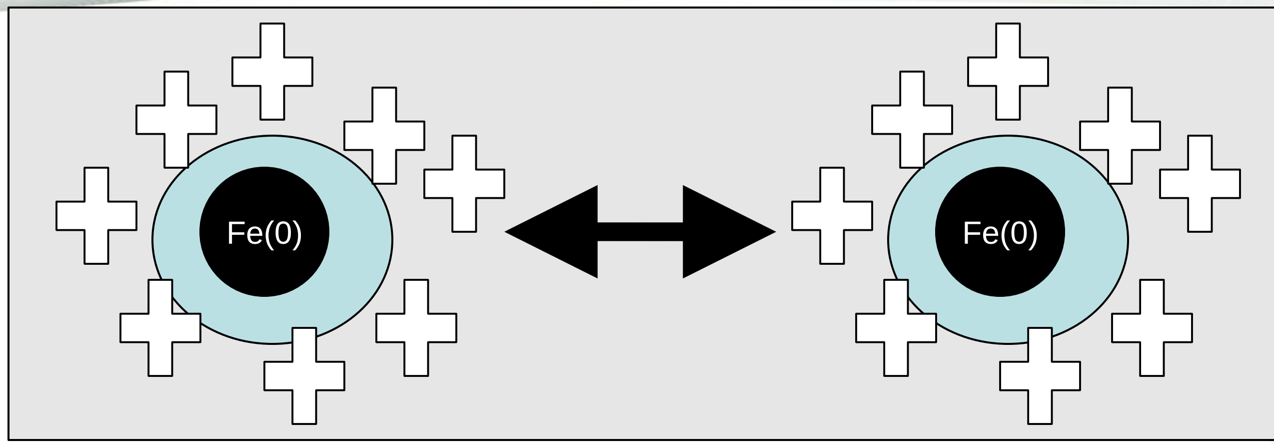
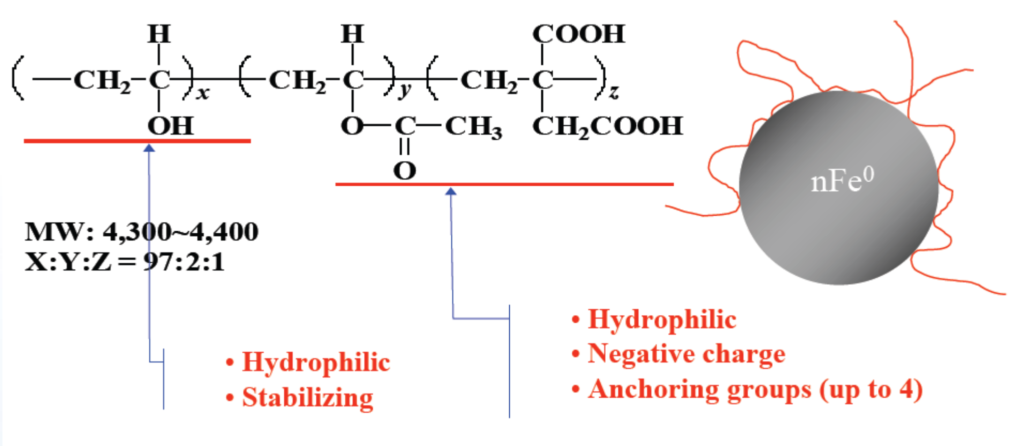
IV. Surface modification options

- Bare nZVI aggregates quickly & migrates poorly
- Dense slurries foster more particle interaction – focus on lower density injections
- Surface modifiers help to maintain surface charge and particle repulsion → stability
- Many surface modifier options: PAA, CMC, HMPA
- Potentially some reactivity loss with the surface modifiers

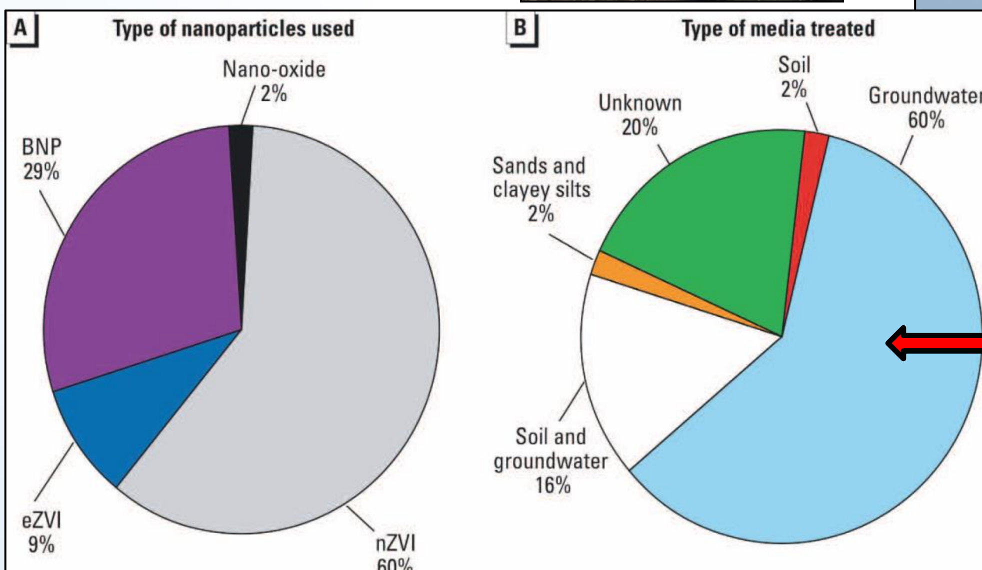




IV. Injection and monitoring

- Unless air stabilized, nZVI is quite reactive (not easily stored)
  - Minimize aging time
- Slurry "strength"
  - 1 g/L ≤ nZVI ≤ 20 g/L (Avg ~10 g/L)
- Delivery methods:
  - Monitoring/Injection wells
  - Traditional Geoprobe™ emplacement
  - Jet injection techniques
  - Hydraulic/pneumatic fracturing
- Verifying efficacy:
  - Appropriate monitoring network
  - Pre- and post-injection sampling
  - Evidence of physical migration, geochemical changes, and contaminant transformation

IV. Field-scale nZVI projects



>70 Field-scale applications (2015)

cVOCs typically the target

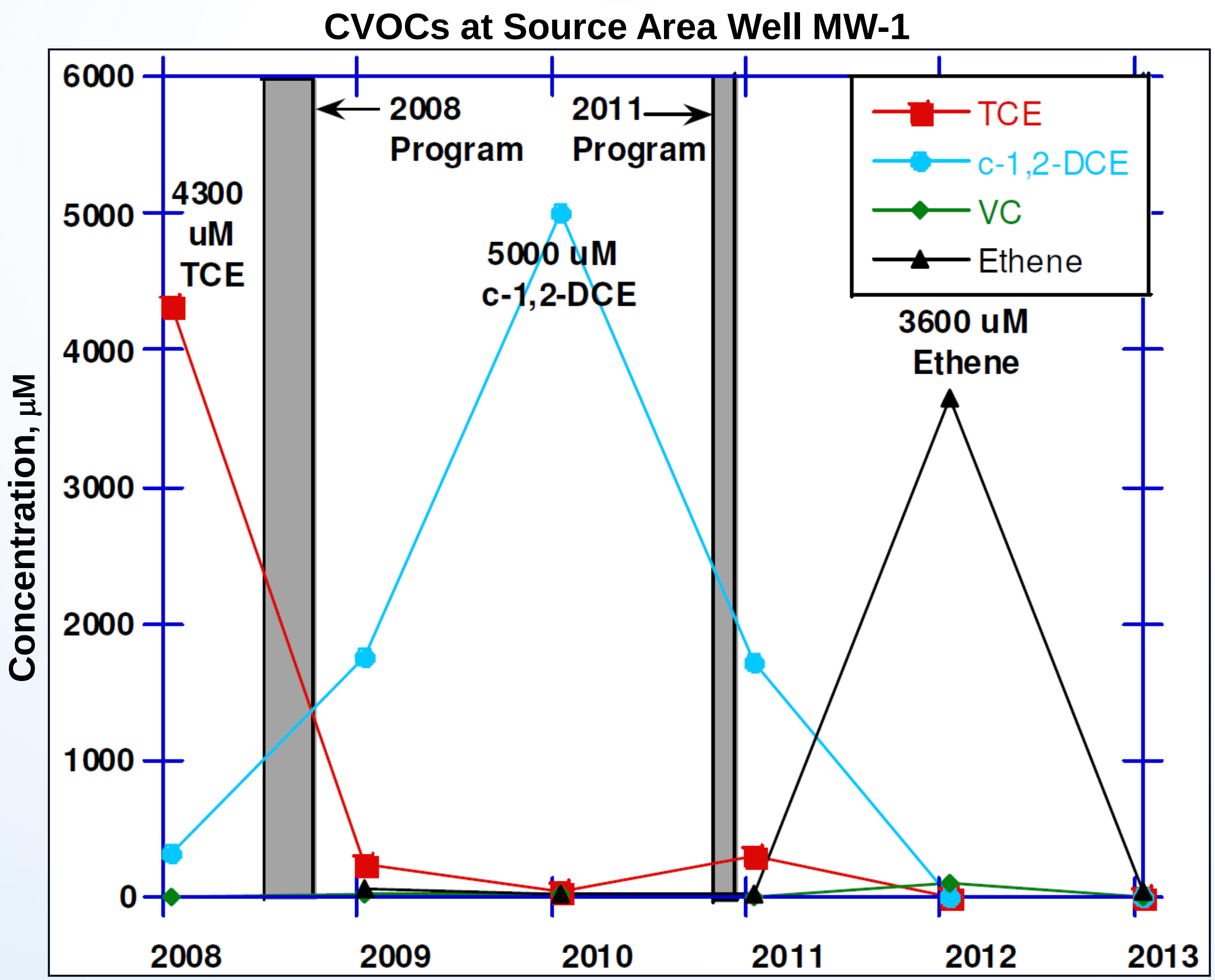
39% PCE, 84% TCE, 55% DCEs, 27% VC

Typically 50-150 kg nZVI, 10-20 g/L

7,375 kg nZVI at Stephenville, TX

Data from Karn et al. (2009) *Environ. Health Perspec*. Vol. 117(12), pp. 1823-1831.

IV. A look at the Stephenville site



Courtesy of Dr. John Freim, On Materials, LLC

Site Overview:

- Active industrial facility
- TCE release from a degreaser
- 30 x 15m source area, 100m dissolved plume
- Source area $[TCE]_{aq}$ ~500 mg/L
- Lithology: 1m coarse fill on native silty sand, depth to groundwater ~2m

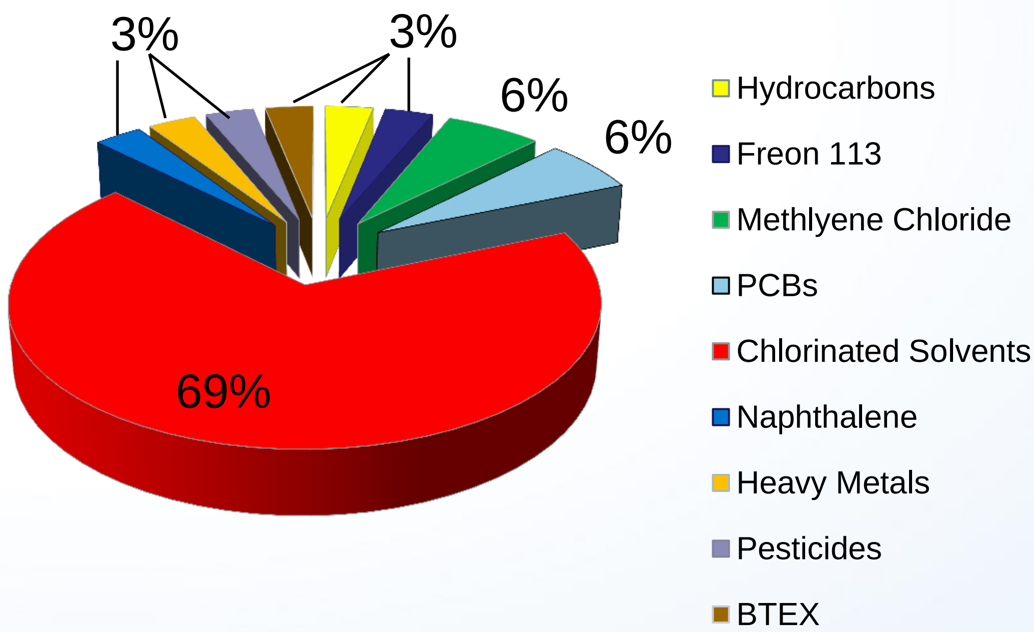
Remediation Program:

- 2008-09: 4,875kg Z-Loy™ nZVI + 43,000kg EVO + 150,000L deoxygenated H_2O
- 60 Injection wells in source area, depth to 3.5m
- 2011: 2,500kg Z-Loy™ + 75,000L EVO slurry + 50L Dhc

IV. Contaminant demographics for nZVI projects

- Chlorinated solvents
  - PCE, TCE, DCE, VC, 1,1,1-TCA
- Freon 113
- Hydrocarbons (C8 to C50)
- Metals (Chromium, nickel)
- Methylene chloride
- Naphthalene
- PCBs
- Pesticides

  (Metolachlor, chlorpyrifos, lindane (γ-HCH)



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Section V

nZVI data needs and future directions

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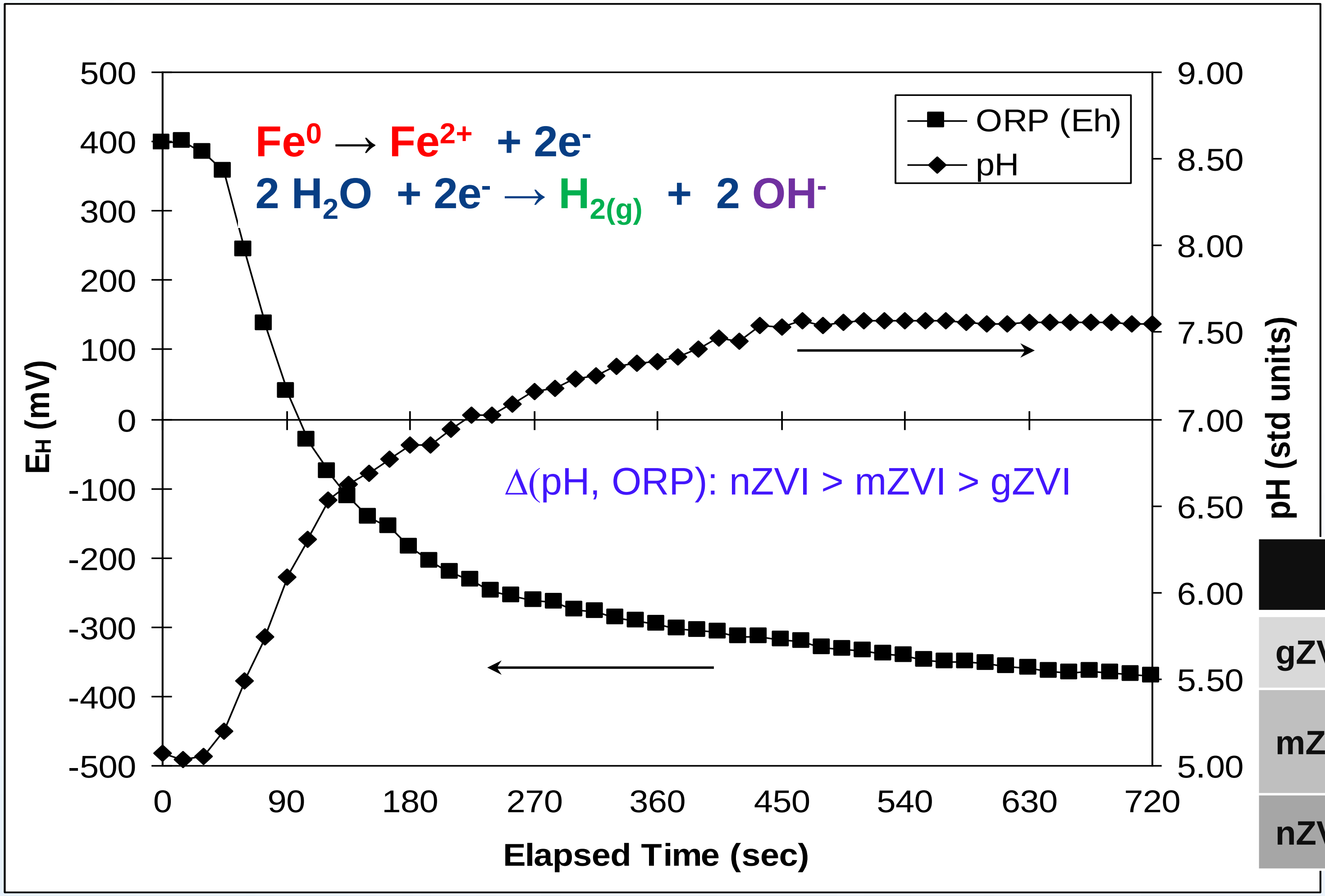
V. Characterization and QA/QC issues

- Need adequate QA/QC for nZVI to assure consistent quality and behavior
  - nZVI is produced from a variety of feedstocks and methods
  - Reactivity, storage, and “born-on dating”
  - Parameters should be relative simple, inexpensive
  - Data furnished by vendors with Safety Data Sheet
- Working list of potential QA/QC parameters:
  - pH and ORP profile in water
  - Particle size distribution (PSD)
  - Specific surface area (m^2/g)
  - Surface charge (zeta potential, isoelectric point)
  - Standard reactivity batch test

V. pH and ORP profile



	ΔpH	ΔORP
gZVI	0-0.5	<300
mZVI	0.5-1.5	300-500
nZVI	1-2.5	>500

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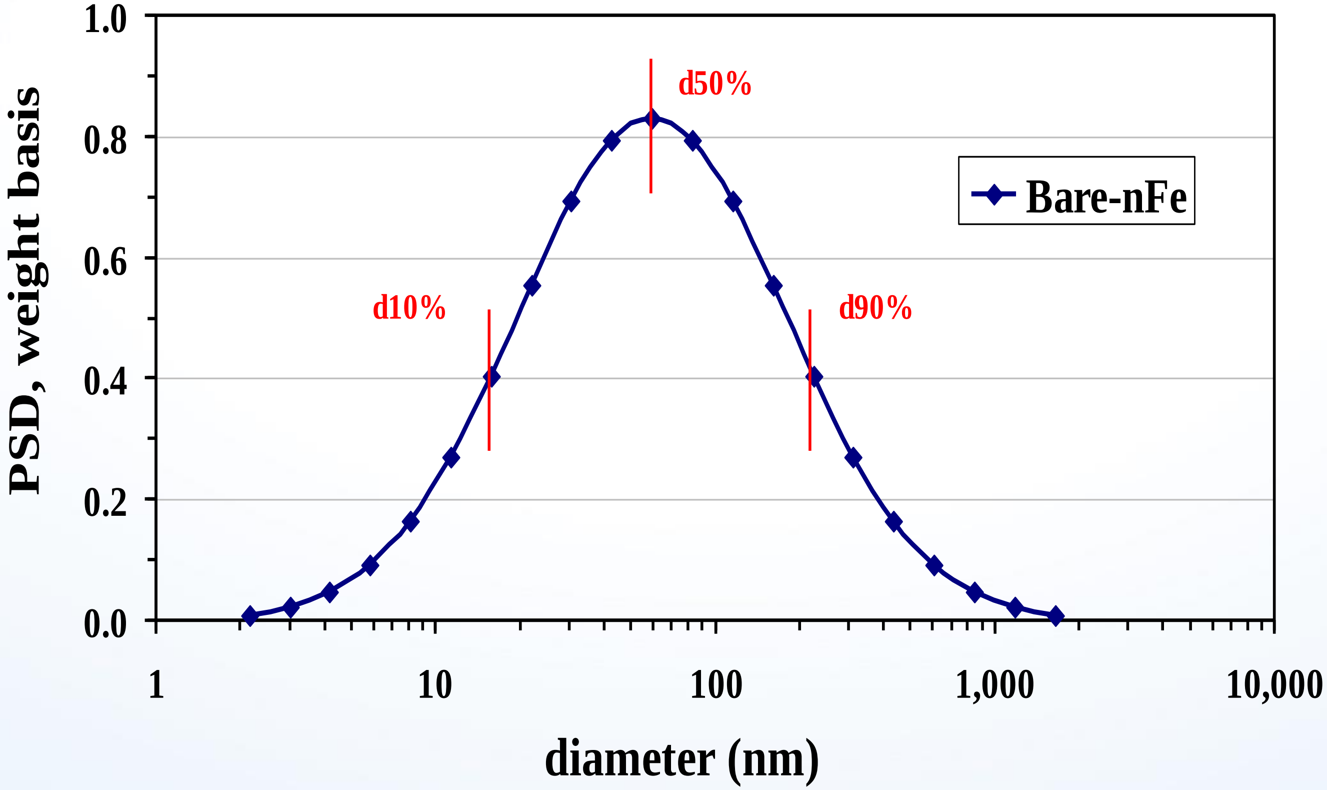
V. Particle size distribution (PSD)



$d_{10\%}$ (nm)	$d_{50\%}$ (nm)	$d_{90\%}$ (nm)
15.8	**59.4**	223.7

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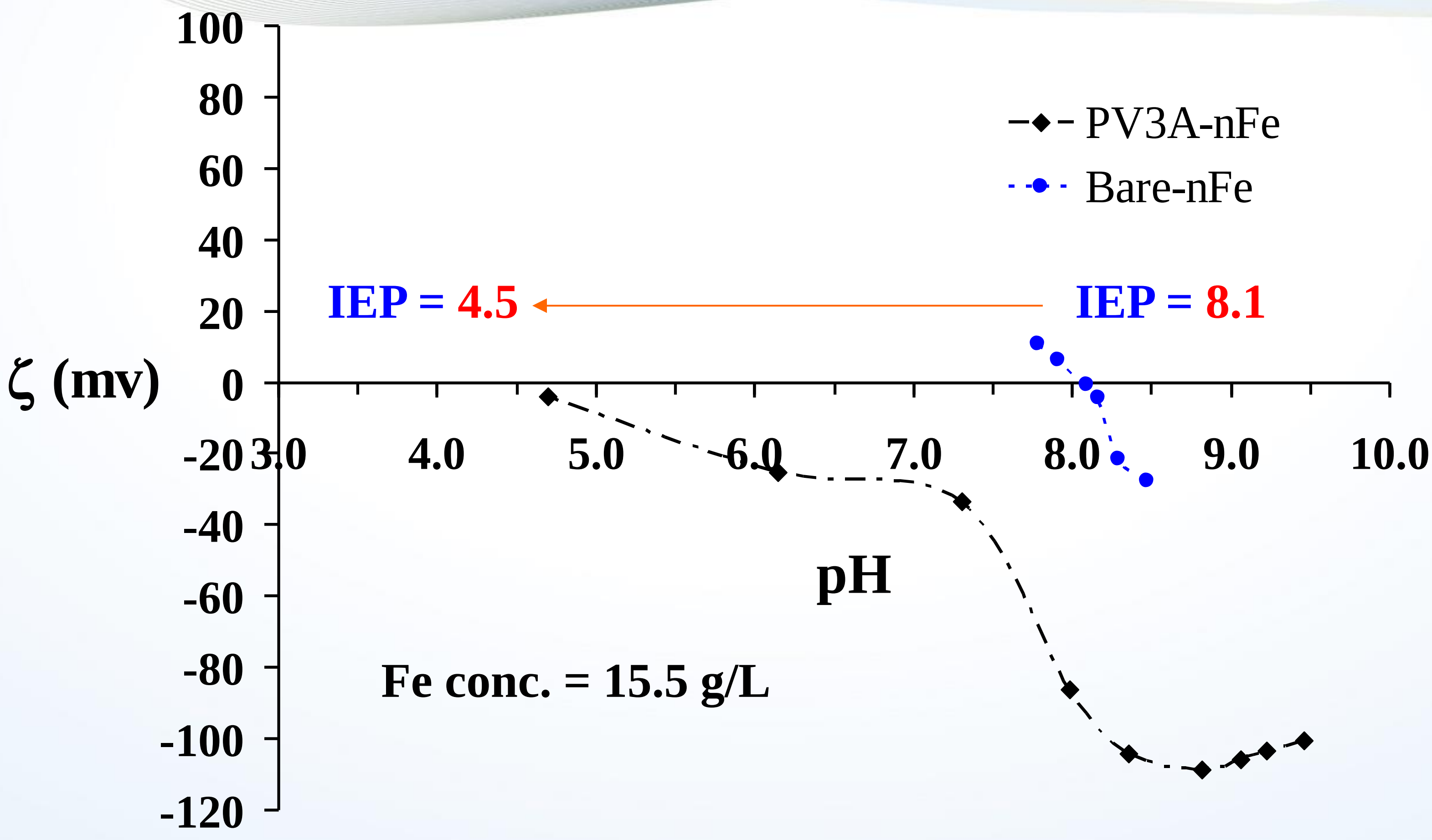
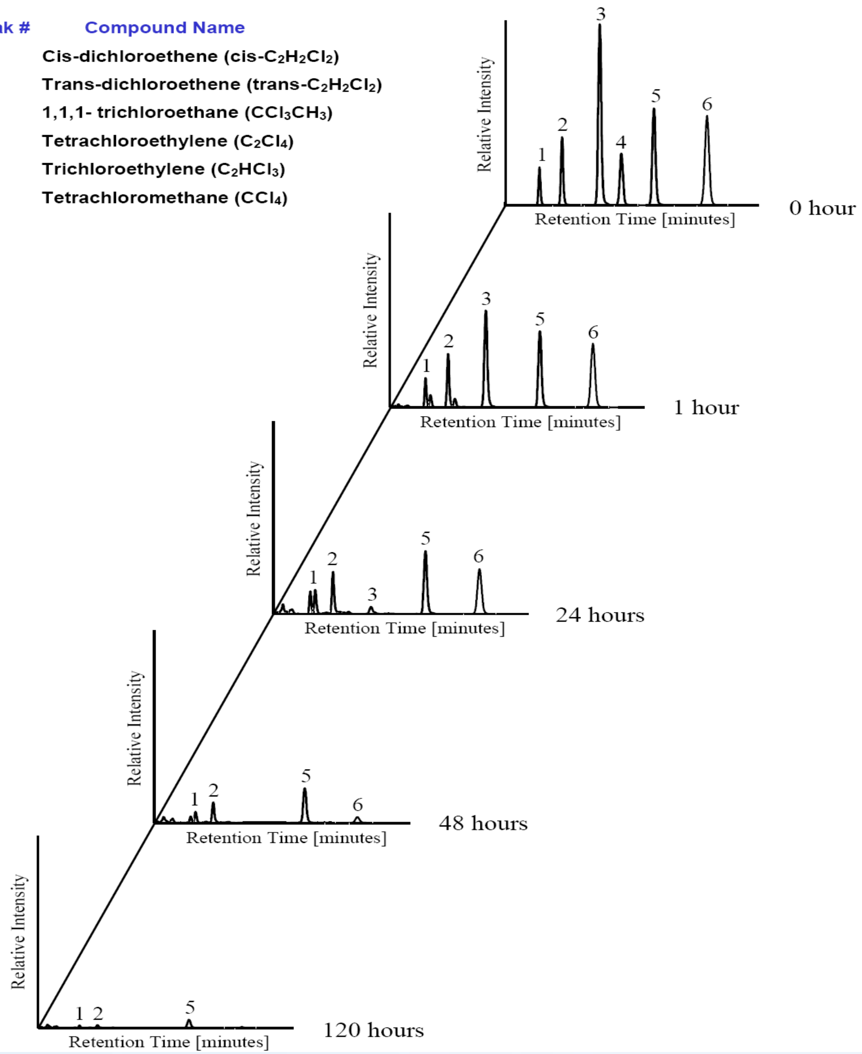
V. Surface charge and stability



More Negative Surface Charge

V. Standard reactivity test

Peak #	Compound Name
1	Cis-dichloroethene (cis-$C_2H_2Cl_2$)
2	Trans-dichloroethene (trans-$C_2H_2Cl_2$)
3	1,1,1- trichloroethane (CCl_3CH_3)
4	Tetrachloroethylene (C_2Cl_4)
5	Trichloroethylene (C_2HCl_3)
6	Tetrachloromethane (CCl_4)



$$C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zFe^{2+} + zCl^-$$

- Aqueous batch reactor
- "Standard" initial contaminant concentration & iron loading
  - ~10 mg/L TCE (or other)
  - 1-5 g/L nZVI
- Track degradation over 1-5 days
- Purpose is to assess the reactivity of the iron, not to characterize the degradation process

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V. R&D & application needs

Materials characterization & deployment

- Stabilize intrinsically reactive nZVI
- Standardized QA/QC
- Lessen variability in production, storage, & deployment

Fate and transport

- nZVI reactive longevity & potential for regeneration
- Selectivity enhancement
- Increase subsurface transport
- Focus on more complex recalcitrant contaminants
- Implications for potential receptors

nZVI effectiveness with other RA technologies

- Couple with bioaugmentation, EK

Site characterization

- Thorough site conceptual models
- Match NPs to site geochemistry, hydrogeology, & contaminants

Applications & costing tools

- Dosage guidance
- Detailed cost-to-cure assessments

Permitting & risk issues

- Normalizing permitting requirements
- Assessing potential exposures
- Balancing remediation requirements, technology capabilities, & risks

V. Pivotal role of… NanoRem

- What is NanoRem?
  - A consortium of 29 partners: universities, national research labs, consultants, and RPs (contaminated site owners)
  - FP7 project
  - 4-yrs beginning April 2013 with €12MM EU funding ($16.8MM)
- Major goals:
  - Identify cost-effective nanotechnology solutions and develop them to commercially relevant scales
  - Determine the fate and transport of these new nanomaterials and assess their capacity to impact receptors
- What it means for nanoremediation:
  - Pivotal opportunity to develop new materials, verify efficacy, and overcome a decade of mixed results and user experiences

NanoRem partners

University of Stuttgart Germany

VEGAS Versuchseinrichtung zur Grundwasser- und Altlastensanierung

KIT Karlsruhe Institute of Technology

SOLVAY asking more from chemistry®

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SciDRE Scientific Instruments Dresden GmbH

UNIVERSITÄT DUISBURG ESSEN

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V. Nanoremediation – the next generation

- **Air stable nZVI,** Fe^0
- **Nano-Goethite**, nFeO(OH)
- **Carbo-iron®**
- **Fe-zeolites**
- Bio-Magnetite, Fe_3O_4
- Biochar-nZVI*
- Barium ferrate**
- Zero-valent magnesium, Mg^0
- Nanoscale calcium peroxide*, CaO_2

Reduction Sorption Oxidation Sequestration

* - Not being investigated as part of NanoRem (2013-2017)
** - Thus far, principally at the research scale

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IV.c. Parting perspectives on nZVI

- It has been an eventful but up-and-down 20 years
  - Burgeoning nZVI academic research globally
  - Field applications have not kept pace (failures, perceived risks, & inadequate cost-benefit data)
- Outlook for the nZVI technology is positive if:
  - NanoRem outcomes are positive (new & better NP technologies, fate & transport data, cost-benefit data, & successful field projects)
  - Need well-designed, large-scale & multi-year projects
  - Practitioners embrace nZVI as a complementary remedial technology
- DWE’s gut feeling:
  - nZVI will evolve but remain a niche player in the remediation practitioner’s quiver of technologies

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V. A mixed track record so far…

- Inadequate site characterization or CSM
  - GW flow direction & hydrogeology not well understood
  - Low K zones or preferential pathways
  - Elevated CO_3^{2-}, pH, or completing electron acceptors, etc.
- Insufficient iron dosing
  - Target post-injection results (Gavaskar, 2005):
    - Iron to saturated soil ratio >0.004
    - Redox potential -400 mV
  - Multiple nZVI injections needed
  - Natural reductant demand too high
- Material availability and quality
- Cost

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