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"Practical Assessment and Optimization of Redox-Based Groundwater Remediation Technologies"

September 8, 2016

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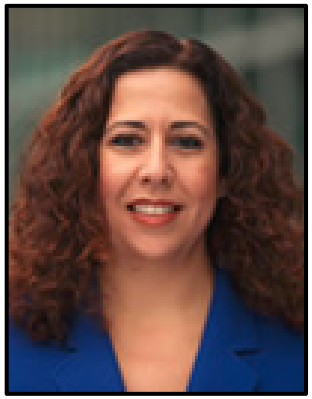
Welcome and Introductions



Rula A. Deeb, Ph.D.
Webinar Program Coordinator

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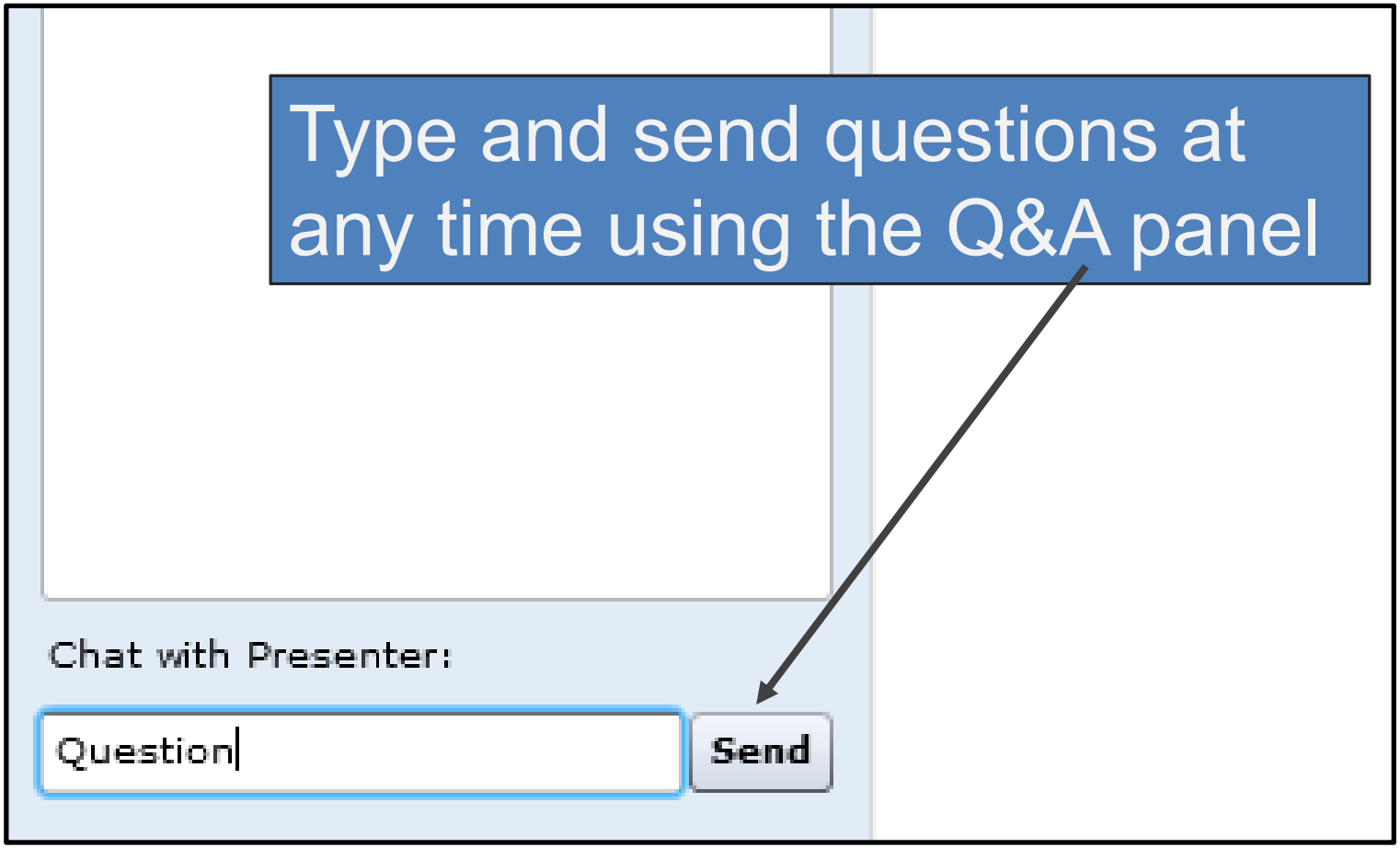
Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Practical Assessment and Optimization of Redox-Based Groundwater Remediation Technologies**
  - **Redox, Background and Challenges** (25 minutes + Q&A)
    Dr. Paul Tratnyek, Oregon Health & Science University
  - **Redox Applications** (25 minutes + Q&A)
    Dr. Richard Johnson, Oregon Health & Science University
- **Final Q&A session**

How to Ask Questions



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- Delays in the broadcast audio
  - Click the mute/connect button
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  - If delays continue, call into the conference line
    - Call into the conference line: 303-248-0285
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- Submit a question using the chat box

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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SERDP

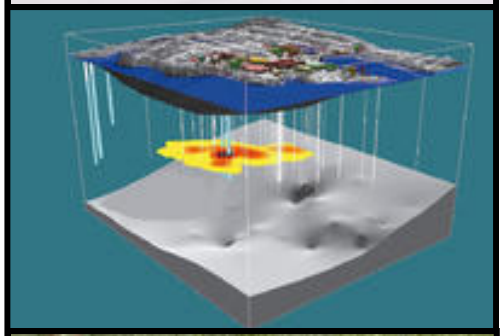
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

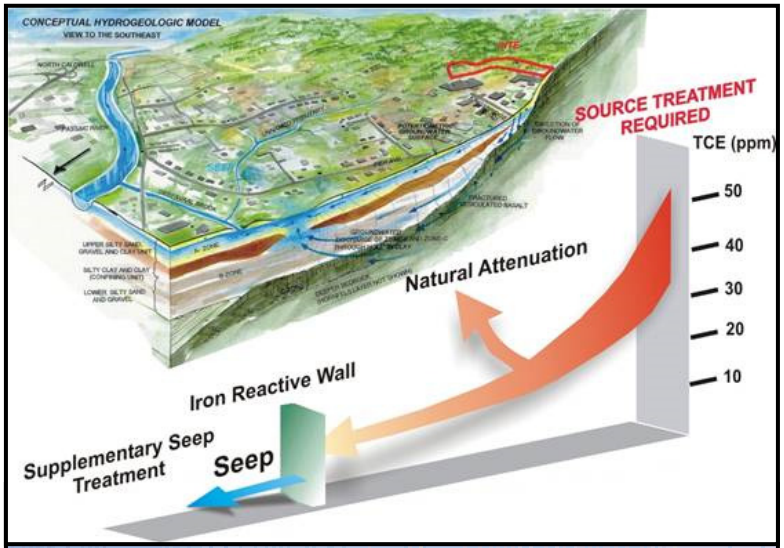
Program Areas

1. Energy and water
2. Environmental restoration
3. Munitions response
4. Resource conservation and climate change
5. Weapons systems and platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



SERDP and ESTCP Webinar Series

Date	Topic
September 22, 2016	Managing the Brown Treesnake Headache: Assessment of the Aerial Acetaminophen Bait Drop on Guam
October 6, 2016	Cyber Security Requirements and Impacts on Installation Energy Systems
October 20, 2016	DoD Decision Making and Climate Change

SERDP and ESTCP Webinar Series

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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Practical Assessment and Optimization of Redox-Based Groundwater Remediation Technologies: ***Redox, Background and Challenges***

Paul Tratnyek, Ph.D.
Oregon Health & Science University

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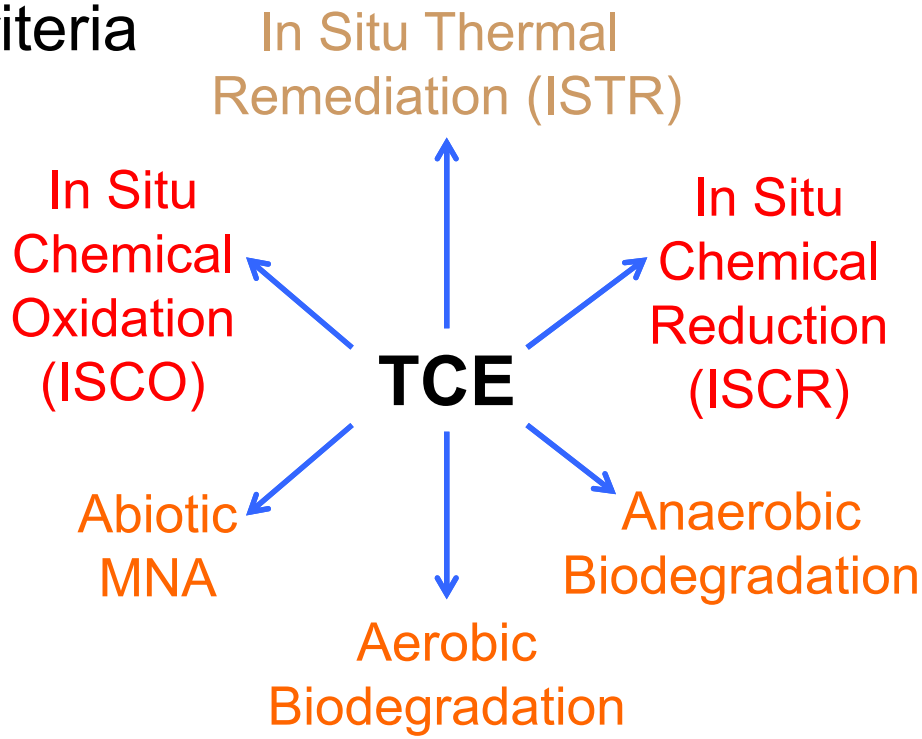
Agenda

- Background and challenges
  - Limitations of traditional methods
  - Advantages of “Chemical Probes” methods
  - Selection of chemical probes (CRPs)
  - Measuring mineral redox potentials
  - Reconciling Platinum (Pt) and chemical probe results
  - Explaining contaminant reduction rates
- Applications (Rick Johnson)

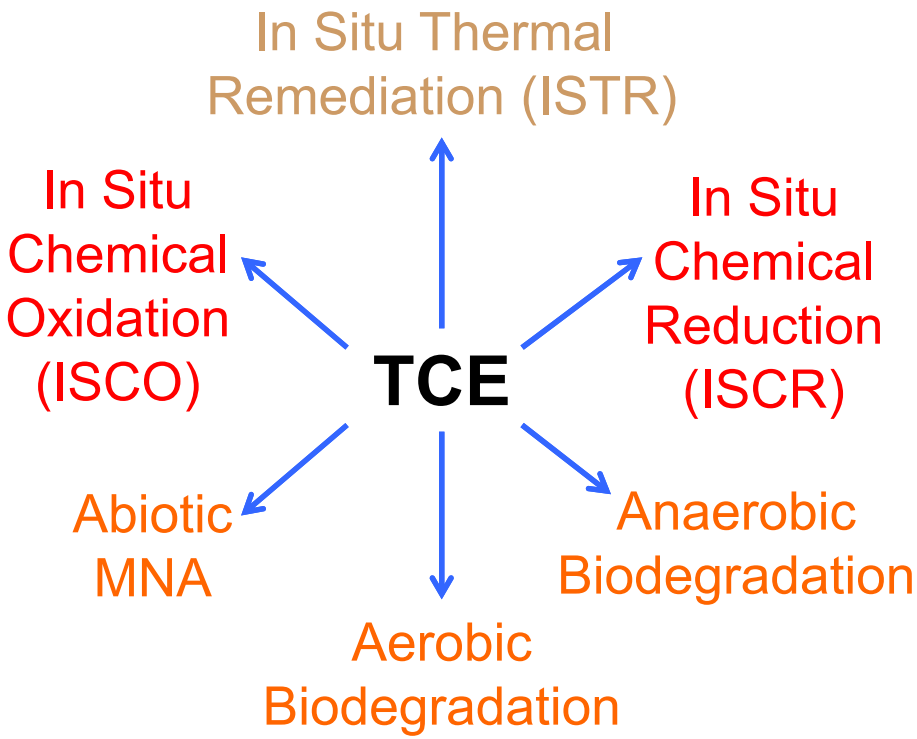
Problem of Redox Characterization

- Almost all approaches to remediation of groundwater contaminated with chlorinated solvents involve oxidation-reduction (redox) reactions
- Many of the assessment criteria used to evaluate these remediation technologies are based on redox concepts



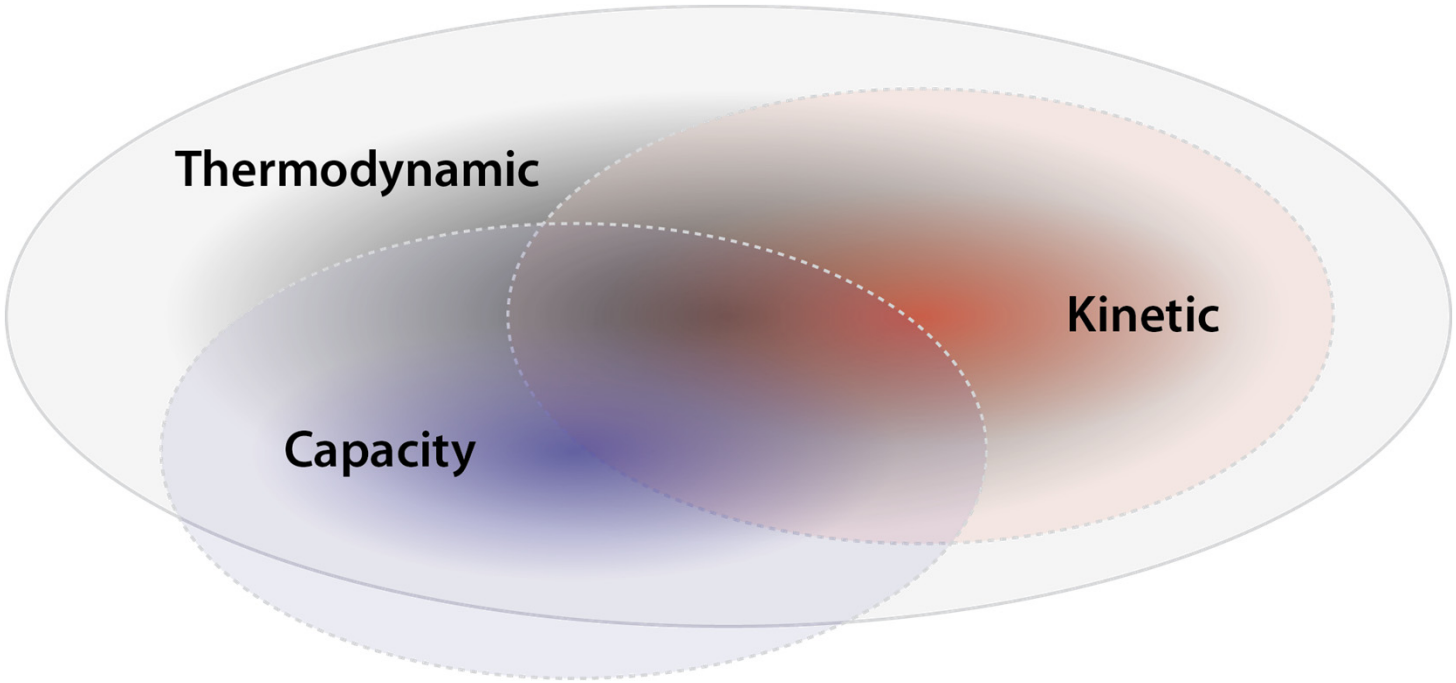
Problem of Redox Characterization

- Existing redox-based assessment criteria [e.g., oxidation-reduction potential (ORP) and natural oxidant demand (NOD)] are not adequate for:
  - Selecting among alternative technologies
  - Optimizing implementation of selected technologies
  - Assessing performance and diagnosing failures



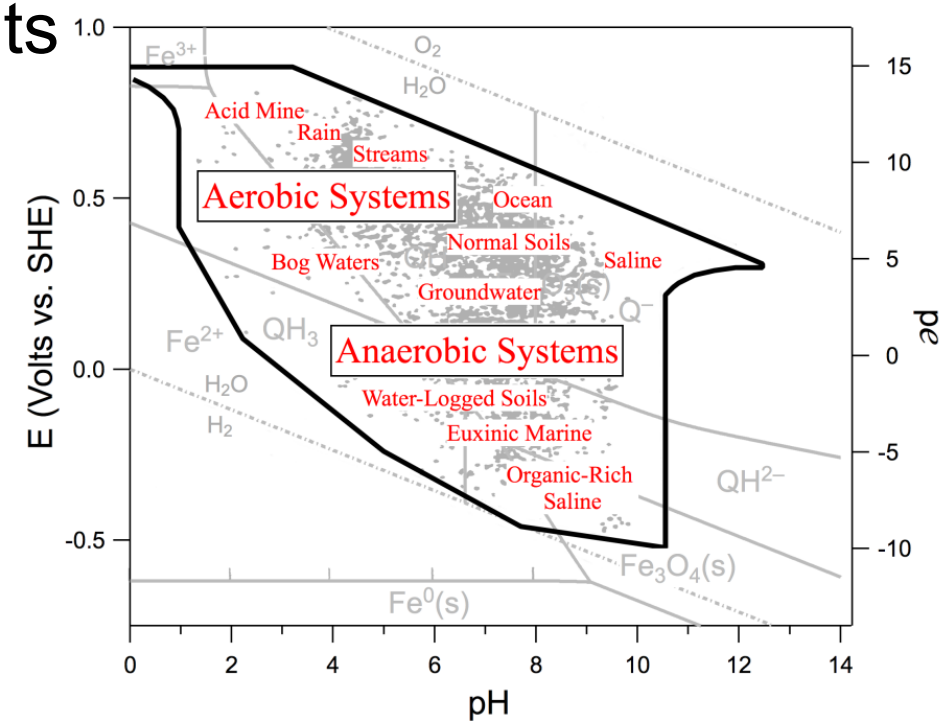
Types of Redox Criteria

- ***Thermodynamic***: Will the desired reactions occur?
- ***Kinetic***: Will they be fast enough?
- ***Capacity***: Will they go far enough?



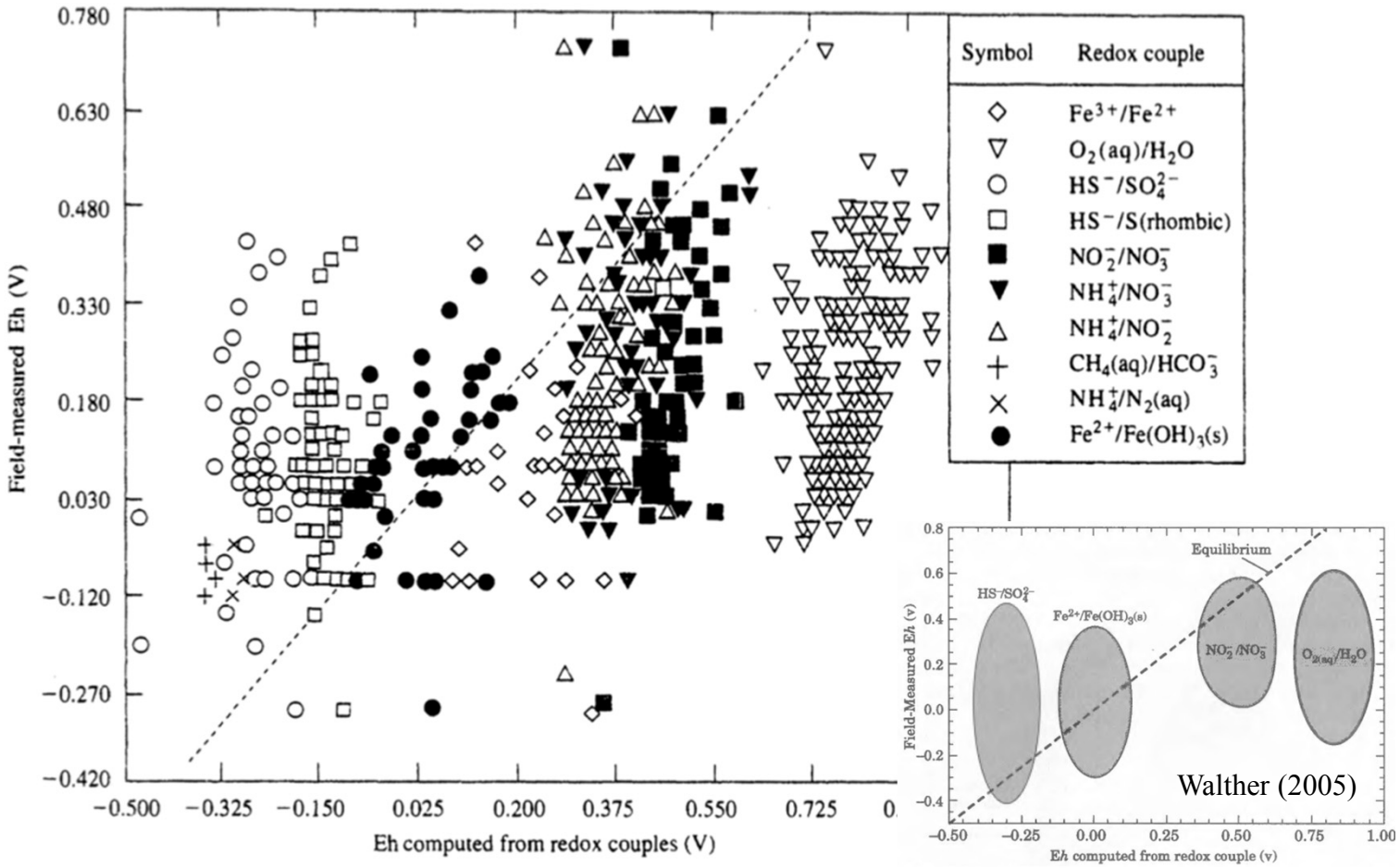
Types of Redox Criteria

- Thermodynamic criteria usually based on:
  - Eh (ORP) by potentiometry with Pt electrode
  - Maybe DO, other TEAPs or dissolved H_2
- Eh and pH measurements (gray dots) correspond only very loosely with major water types
- Inconsistencies are common due to kinetic barriers to reaction between redox couples



Tratnyek et al. (2011) Ch. 1 . In: Aquatic Redox Chemistry ACS Symp. Ser. Vol. 1071

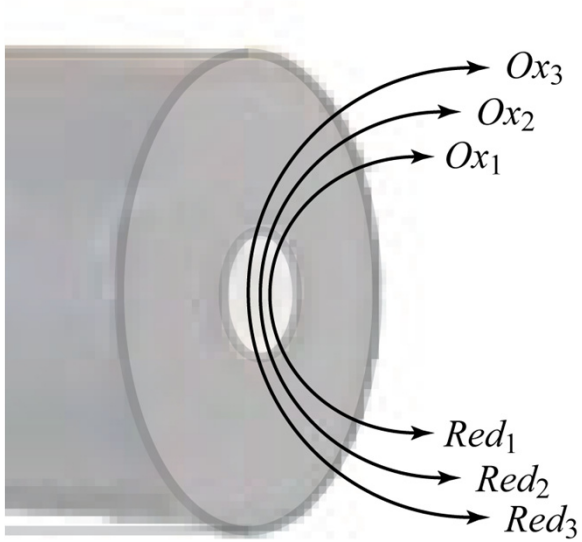
Interpretation of ORP



Lindberg (1984); Adapted in Langmuir (1997)

Interpretation of ORP

Working Electrode (Pt, GC)



$$\mathrm{Ox}_i + a\mathrm{H}^+ + n\mathrm{e}^- \rightleftharpoons \mathrm{Red}_i$$

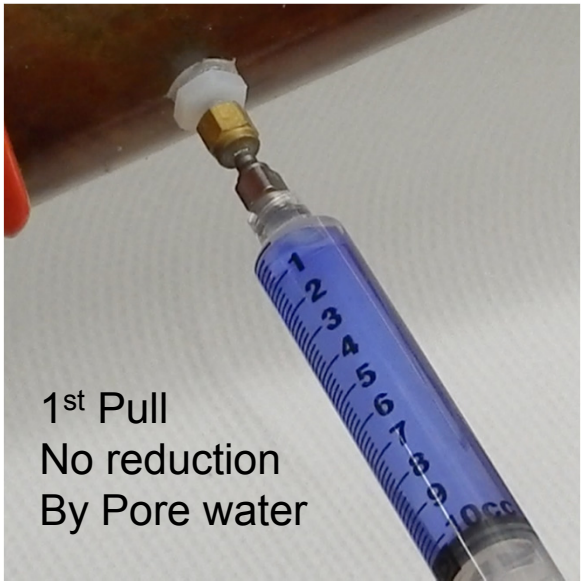
for all electrode-active half-reactions

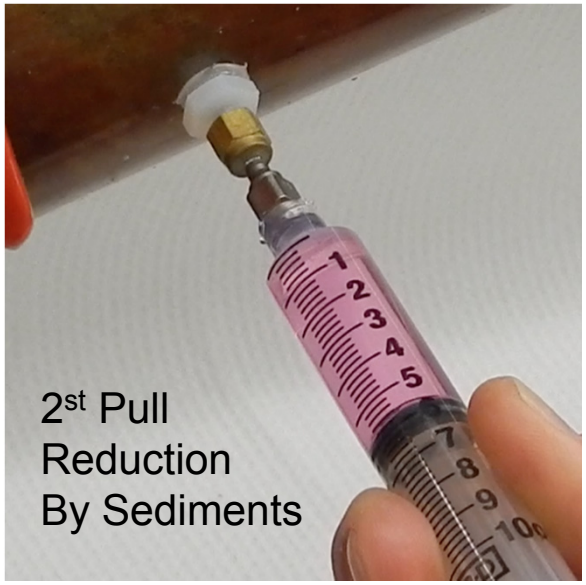
$$E_{mix} = \sum_{i=1}^{m} \frac{\left|i_i^0\right|}{\sum\left|i_i^0\right|} E_i^0 - \frac{\mathrm{R}T}{n_i\mathrm{F}} \ln \frac{\{Red_i\}}{\{Ox_i\}\{H^+\}^a}$$

Shi et al. (2011). Environ. Sci. Technol. 45: 1586-1592

Interpretation of ORP

- Resazurin, because it is most easily reduced
- Purple (oxidized) to Pink (reduced)
- Irreversible, convenient for push-pull
- Documented with movie on YouTube and in a SERDP blog post





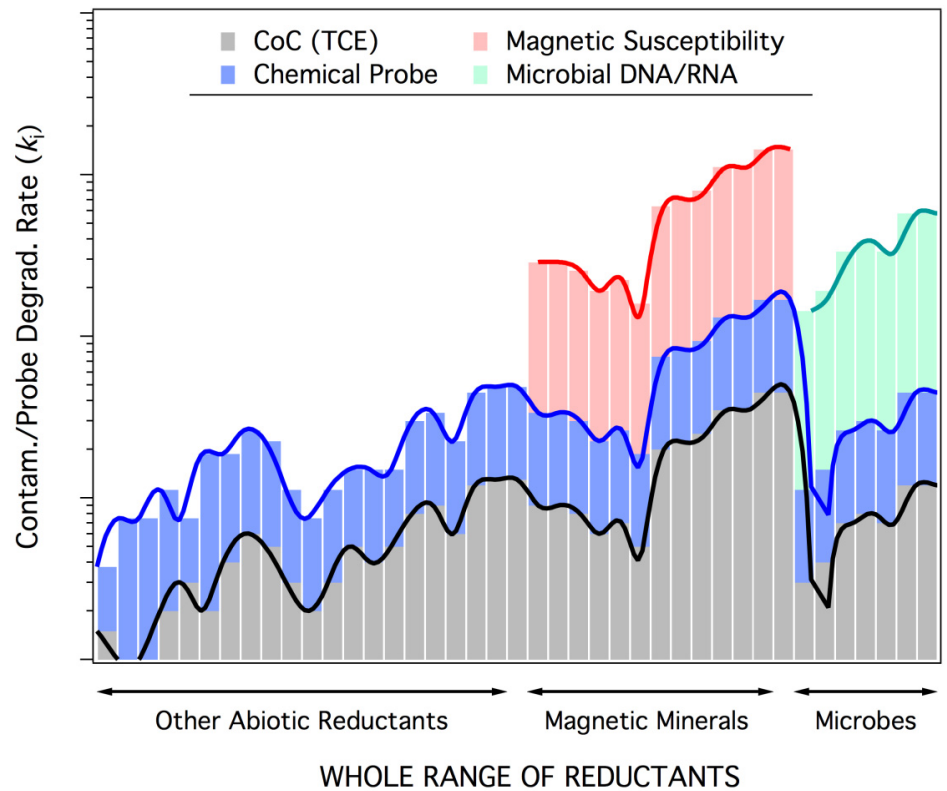
https://www.serdp-estcp.org/News-and-Events/Blog/Practical-Assessment-of-Redox-Based-Groundwater-Remediation-Technologies

Objectives of ER-2308

- Overall objective
  - Develop and demonstrate a suite of diagnostic tools for assessment and optimization of redox-based remediation technologies for aquifers contaminated with chlorinated hydrocarbons
- Specific objectives
  - (Re)evaluate traditional redox-based characterization methods
  - Develop new in situ, redox characterization methods based on chemical probes and push-pull methods
  - Quantitatively define the relationship between probe characterization methods and the actual performance of redox-based remedies applied to particular sites

Approach

- Current characterization methods (e.g., ORP) do not represent the whole range of environmental reductants
- Chemical probes may have a "response curve" more like contaminants
- New approach based on chemical redox or reactivity probes (CRPs)



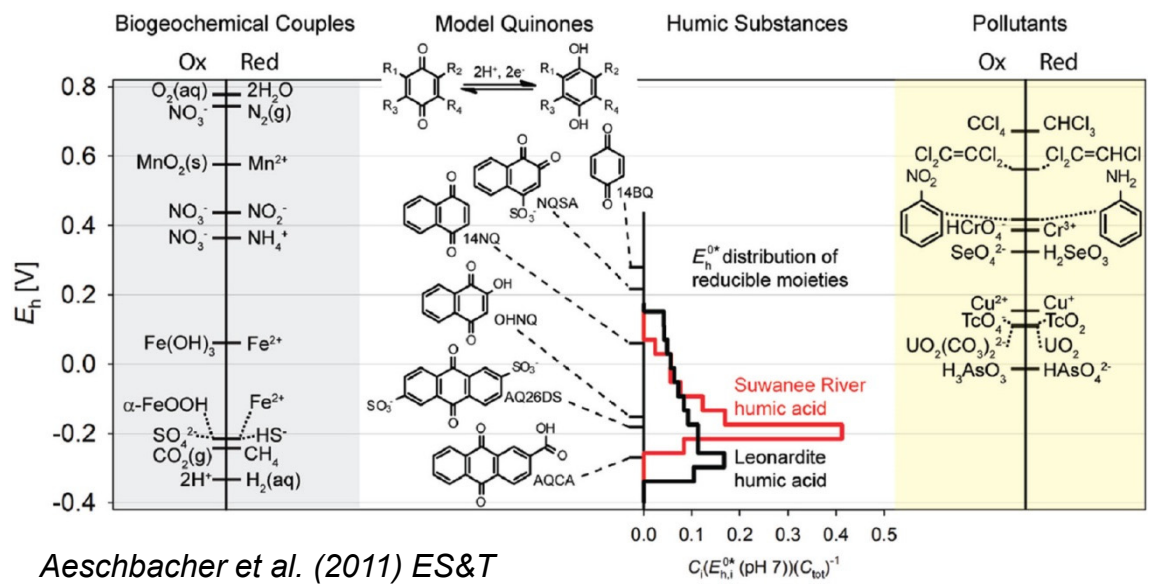
CRP Selection

- Resorufin
  - RSF
- Indigo-2,6-disulfonate
  - I2S
- Anthraquinone-2,6-disulfonate
  - AQDS
- Anthraquinone-2-sulfonate
  - AQS

Table 1. Thermodynamic constants for six redox indicators[a]

Name	E_{m7}[b]	pK_{o1}[c]	pK_{r1}[d]	pK_{r2}[e]
2,6-Dichloro-indo-phenol	+217	5.7	7.0	10.1
2,6-Dichloro-indo-*o*-cresol	+181	5.5	7.1	10.4
Indigo-5,5′,7,7′-tetrasulfonate	−46	11.9	7.0	11.8
Resorufin	−51	[f]	[f]	[f]
Indigo-5,5′,7-trisulfonate	−81	11.7	7.2	12.1
Indigo-5,5′-disulfonate	−125	12.3	7.4	12.1

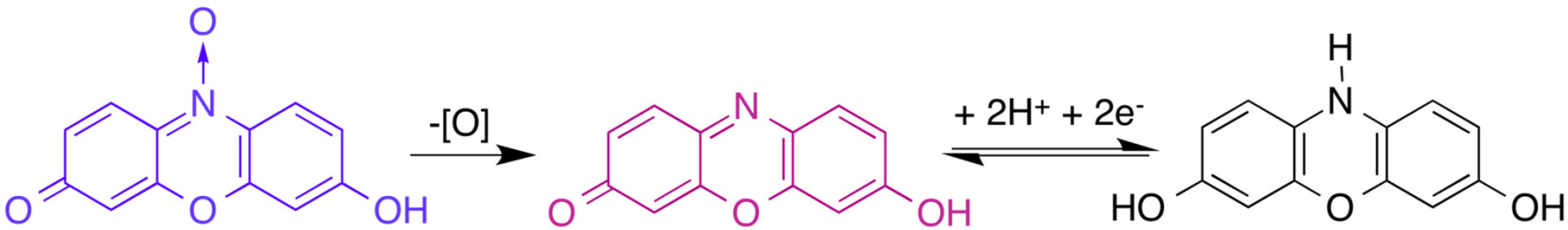
Tratnyek and Wolfe (1989) ET&C

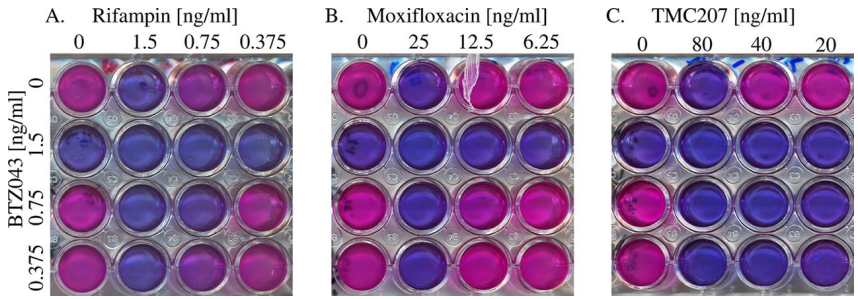


Aeschbacher et al. (2011) ES&T

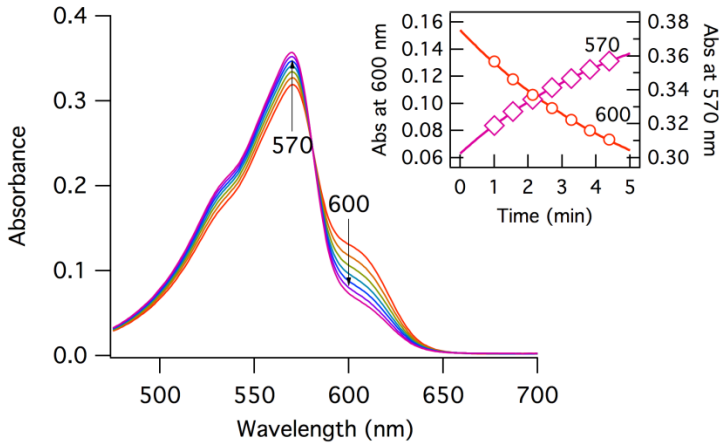
CRP Selection

Resazurin and Resorufin Probe/Indicators (RSZ, RSF)



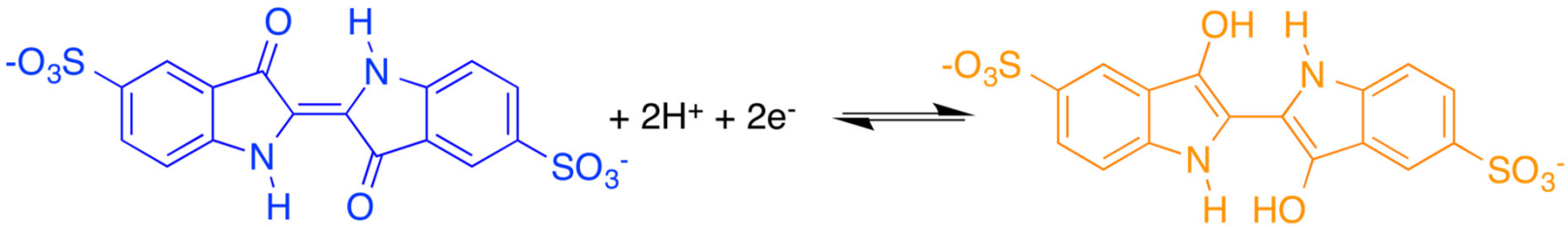


Common Assay for Cell Viability



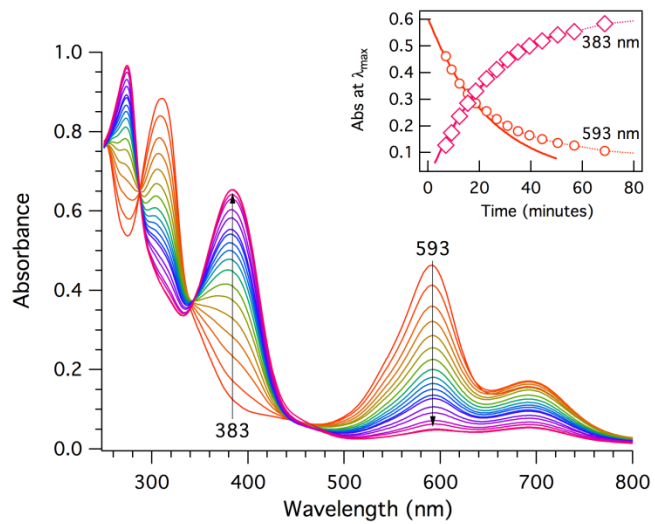
CRP Selection

Indigo Sulfonate Probe/Indicator (I2S)



Indigo Disulfonate
Blue (610 nm)

Dihydro Indigo Disulfonate
Yellow (407 nm)



Quantitative Application

- Calculate Eh from CRP data (ECRP)

$$\mathrm{CRP_{ox}} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{CRP_{red}} + \mathrm{H_2O}$$

- In general

$$E_{\mathrm{CRP}} = E^0 + \frac{\mathrm{R}T}{2\mathrm{F}} \ln\left(\left[\mathrm{H^+}\right]^2 + K_{\mathrm{r1}}\left[\mathrm{H^+}\right] + K_{\mathrm{r1}}K_{\mathrm{r2}}\right) + \frac{\mathrm{R}T}{2\mathrm{F}} \ln\left(\frac{\left[\mathrm{CRP_{ox}}\right]}{\left[\mathrm{CRP_{red}}\right]}\right)$$

- At pH 7

$$E_{\mathrm{CRP}} = E_7^0 + \frac{\mathrm{R}T}{2\mathrm{F}} \ln\left(\frac{\left[\mathrm{CRP}_{ox}\right]}{\left[\mathrm{CRP}_{red}\right]}\right)$$

- Cf. E^0 for minerals, E_{Pt} (ORP), E_{OCP}, etc.

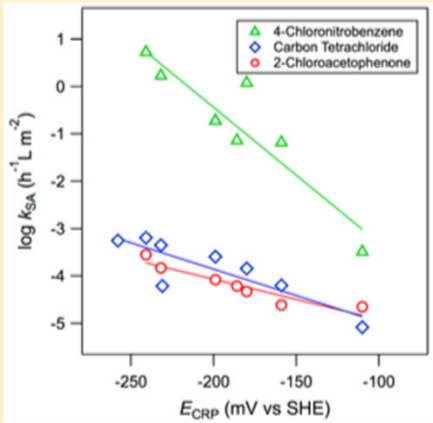
Results • Minerals vs. CoCs

Chemical Reactivity Probes for Assessing Abiotic Natural Attenuation by Reducing Iron Minerals

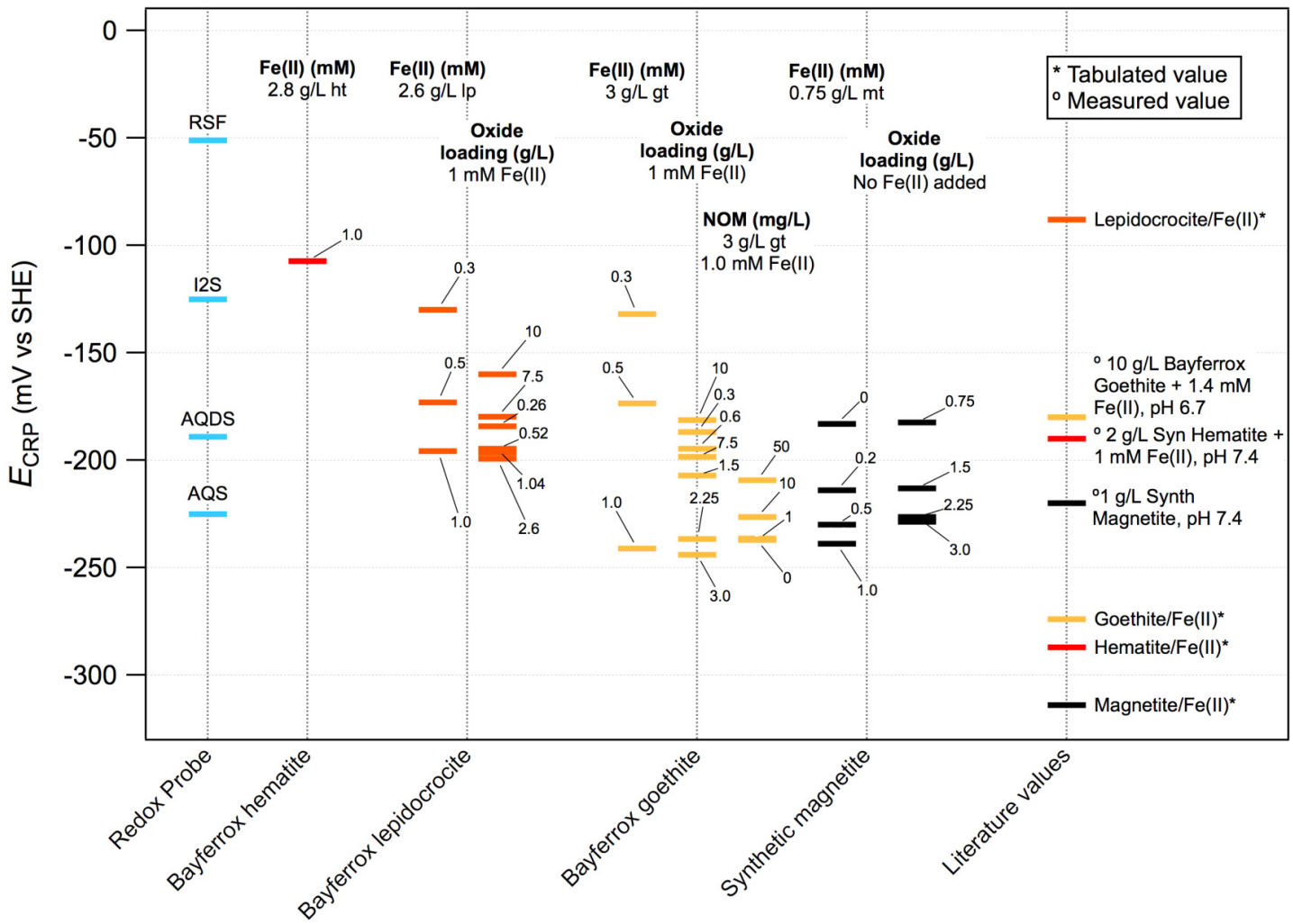
Dimin Fan,[†] Miranda J. Bradley, Adrian W. Hinkle, Richard L. Johnson, and Paul G. Tratnyek*

Environ. Sci. Technol. 2016, 50(4): 1868-1876
[DOI: 10.1021/acs.est.5b05800]

ABSTRACT: Increasing recognition that abiotic natural attenuation (NA) of chlorinated solvents can be important has created demand for improved methods to characterize the redox properties of the aquifer materials that are responsible for abiotic NA. This study explores one promising approach: using chemical reactivity probes (CRPs) to characterize the thermodynamic and kinetic aspects of contaminant reduction by reducing iron minerals. Assays of thermodynamic CRPs were developed to determine the reduction potentials (E_{CRP}) of suspended minerals by spectrophotometric determination of equilibrium CRP speciation and calculations using the Nernst equation. E_{CRP} varied as expected with mineral type, mineral loading, and Fe(II) concentration. Comparison of E_{CRP} with reduction potentials measured potentiometrically using a Pt electrode (E_{Pt}) showed that E_{CRP} was 100−150 mV more negative than E_{Pt}. When E_{Pt} was measured with small additions of CRPs, the systematic difference between E_{Pt} and E_{CRP} was eliminated, suggesting that these CRPs are effective mediators of electron transfer between mineral and electrode surfaces. Model contaminants (4-chloronitrobenzene, 2-chloroacetophenone, and carbon tetrachloride) were used as kinetic CRPs. The reduction rate constants of kinetic CRPs correlated well with the E_{CRP} for mineral suspensions. Using the rate constants compiled from literature for contaminants and relative mineral reduction potentials based on E_{CRP} measurements, qualitatively consistent trends were obtained, suggesting that CRP-based assays may be useful for estimating abiotic NA rates of contaminants in groundwater.

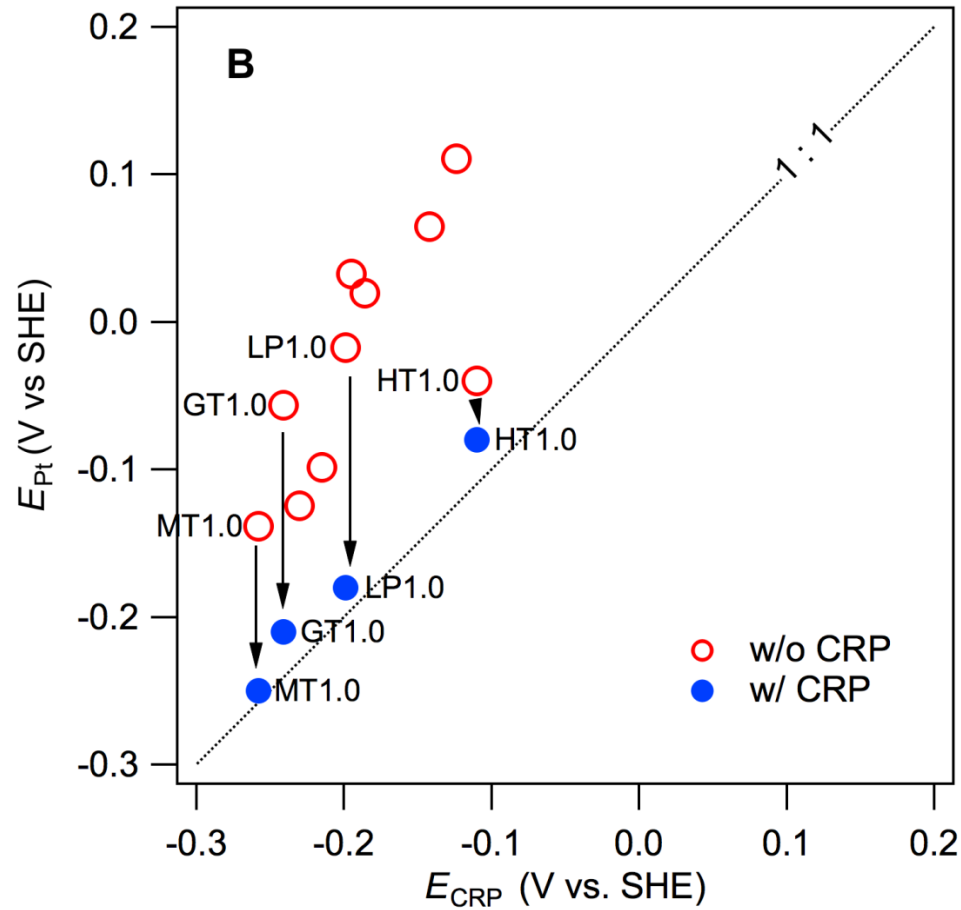


Results • Minerals vs. CoCs



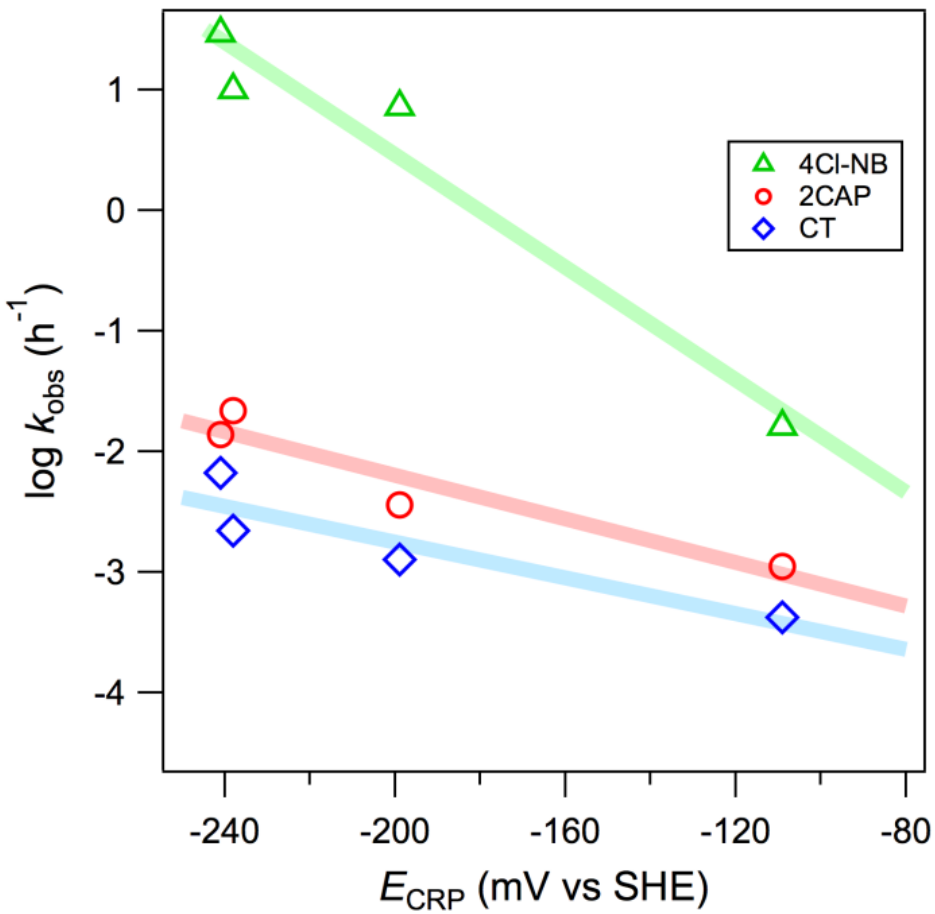
Results • Minerals vs. CoCs

- Methods
  - E_{CRP} by CRP with spectrophotometry
  - E_{Pt} by Pt electrode (only)
  - $E_{Pt/CRP}$ by Pt electrode with CRP (10 μM)
- Results
  - E_{Pt} w/o higher than E_{CRP}
  - E_{Pt} w/ CRP ≈ E_{CRP}
  - CRP mediates between mineral and electrode



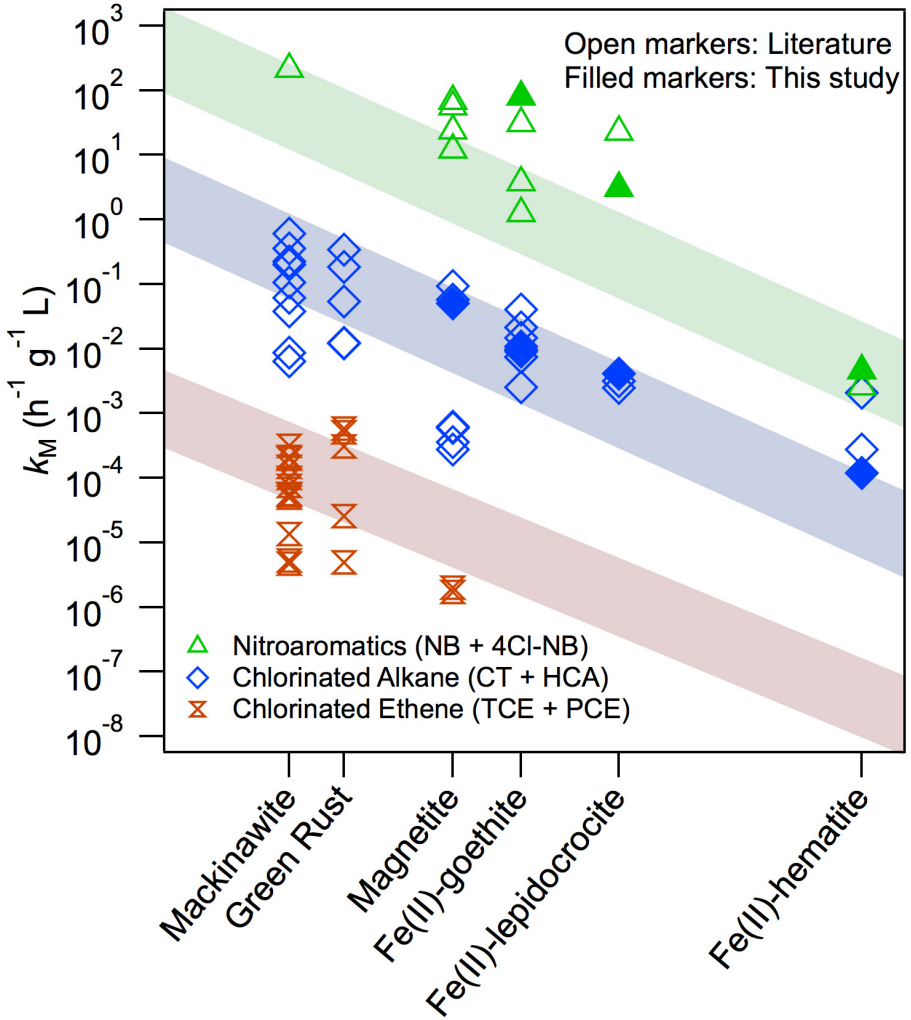
Results • Minerals vs. CoCs

- Methods
  - E_{CRP} by CRP with spectrophotometry
  - k_{obs} by batch and GC
- Results
  - 4Cl-NB >> 2CAP > CT
  - *k*'s correlate with *E*'s
  - Intercepts vary with CoC
  - Future QSARs?



Results • Minerals vs. CoCs

- Extend correlations to include literature data
  - Three classes of CoCs
  - Mass normalized (k_M)
  - Log k_M vs. mineral type
- Trends
  - Nitroaromatics >> Chloro-ethanes >> Chloroethenes
  - Colored bands are not fitted QSARs (yet)
  - Predictions consistent with other SERDP projects



Key Points

- The problem of redox assessment
  - Almost all remediation is redox
  - Methods for characterizing in situ redox (e.g., ORP) are inadequate
  - Need to cover thermodynamic, kinetic and capacity aspects
- Alternative approach
  - Use chemical redox/reactivity probes (CRPs)
  - Several (RSZ and I2S) meet fundamental and practical requirements
  - Complementary to ORP but better penetration, equilibration, etc.
- Batch test results with iron oxides
  - Calculated E_{CRP} with CRP data and Nernst Equation
  - To make ORP measurements match, add CRP as mediator
  - Contaminant reduction rates correlate with E_{CRP}
  - Ranking iron oxides with E_{CRP} predicts relative contaminant reactivity

Q&A Session 1

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Practical Assessment and Optimization of Redox-Based Groundwater Remediation Technologies: ***Redox Applications***

Richard Johnson, Ph.D.
Oregon Health & Science University

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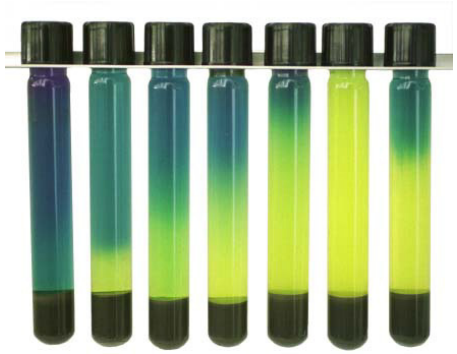
Presentation Outline

- Redox applications
  - CRPs, ISCR, kinetics, capacity
  - Example #1
    - Field characterization of nZVI
  - Example #2
    - Sulfidation for enhanced selectivity
  - Looking ahead

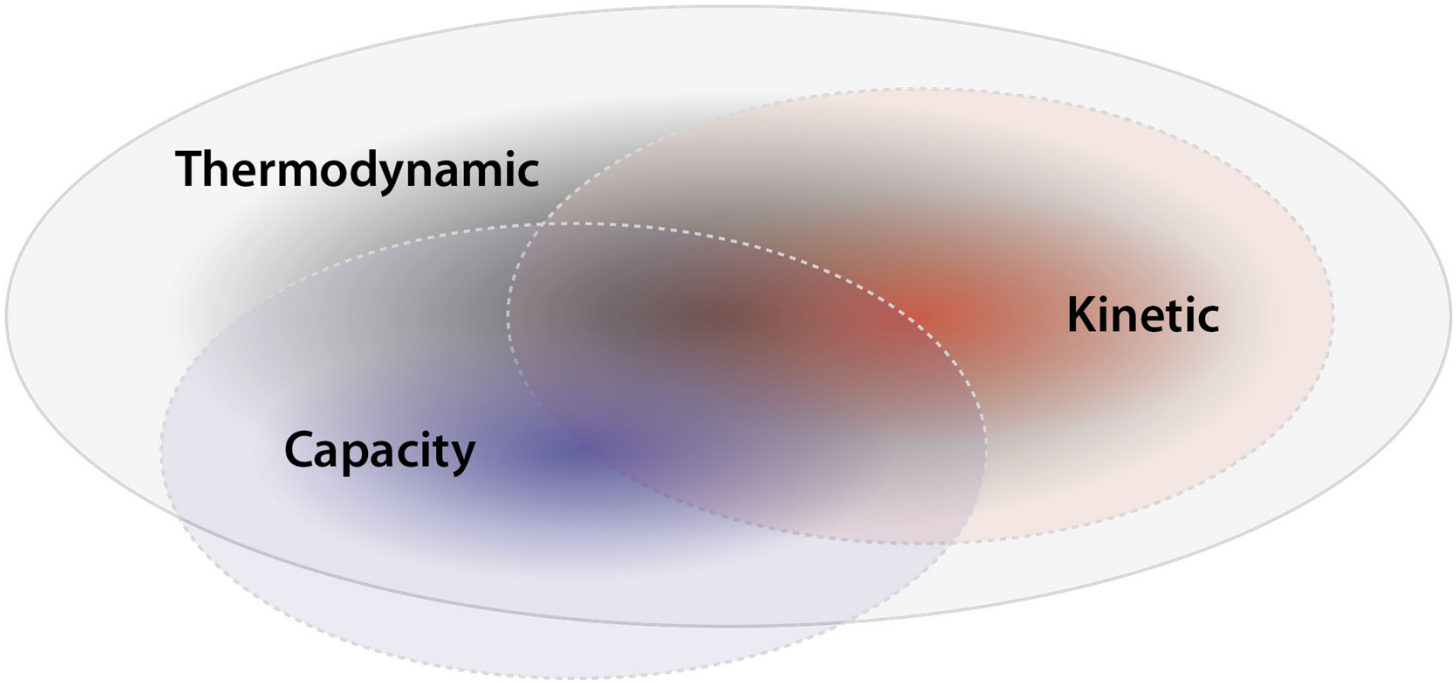
Chemical Reactivity/Redox Probes

- Range of redox indicator dyes
- Key for understanding kinetics and capacity
- CRP choices provide selectivity
- Can be coupled with other probes
- Broadly applicable for redox assessment



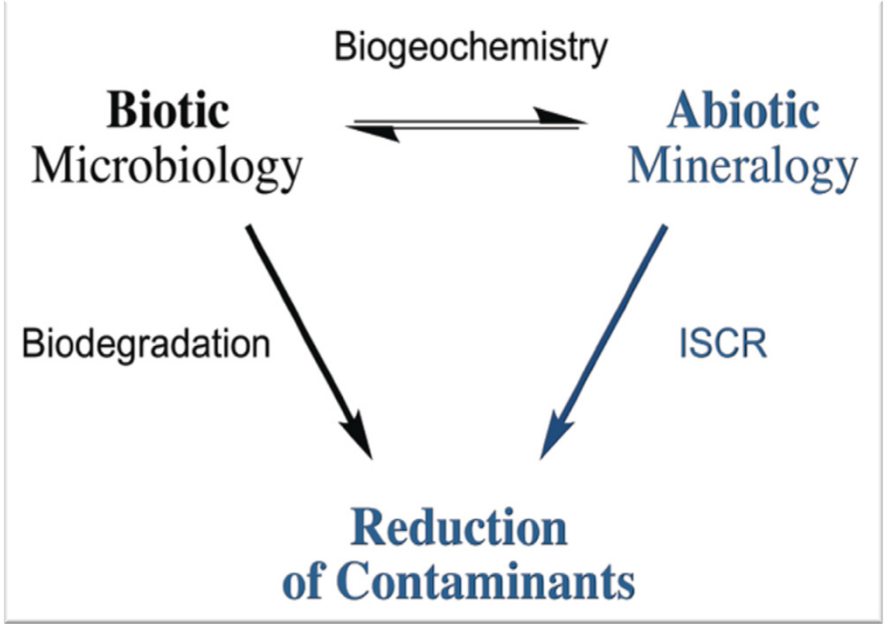
Types of Redox Criteria

- ***Thermodynamic***: Will desired reactions occur?
- ***Kinetic***: Will they be fast enough?
- ***Capacity***: Will they go far enough?



In Situ Chemical Reduction (ISCR)

- Emphasis on abiotic processes
- Microbial activity can play a role
- e.g., sulfate reduction to sulfide



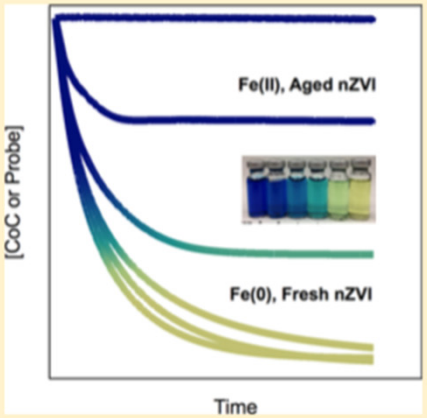
ISCR Kinetics and Capacity

Field Deployable Chemical Redox Probe for Quantitative Characterization of Carboxymethylcellulose Modified Nano Zerovalent Iron

Dimin Fan,[†] Shengwen Chen,[‡] Richard L. Johnson,[†] and Paul G. Tratnyek*[,†]

Environ. Sci. Technol. 2015, 49, 10589−10597
DOI: 10.1021/acs.est.5b02804

ABSTRACT: Nano zerovalent iron synthesized with carboxymethylcelluose (CMC-nZVI) is among the leading formulations of nZVI currently used for in situ groundwater remediation. The main advantage of CMC-nZVI is that it forms stable suspensions, which are relatively mobile in porous media. Rapid contaminant reduction by CMC-nZVI is well documented, but the fate of the CMC-nZVI (including "aging" and "reductant demand") is not well characterized. Improved understanding of CMC-nZVI fate requires methods with greater specificity for Fe(0), less vulnerability to sampling/recovery artifacts, and more practical application in the field. These criteria can be met with a simple and specific colorimetric approach using indigo-5,5′-disulfonate (I2S) as a chemical redox probe (CRP). The measured stoichiometric ratio for reaction between I2S and nZVI is 1.45 ± 0.03, suggesting complete oxidation of nZVI to Fe(III) species. However, near pH 7, reduction of I2S is diagnostic for Fe(0), because aqueous Fe(II) reduces I2S much more slowly than Fe(0). At that pH, adding Fe(II) increased I2S reduction rates by Fe(0), consistent with depassivation of nZVI, but did not affect the stoichiometry. Using the I2S assay to quantify changes in the Fe(0) content of CMC-nZVI, the rate of Fe(0) oxidation by water was found to be orders of magnitude faster than previously reported values for other types of nZVI.

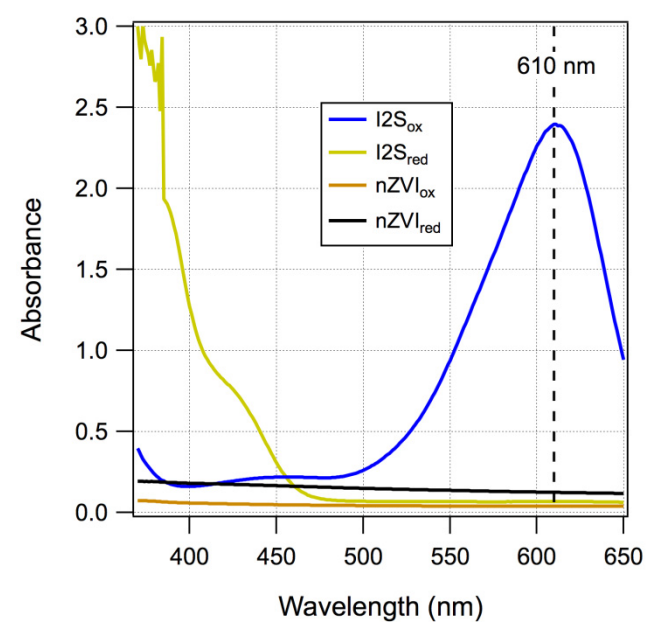


Field Measurement of nZVI

- Redox-sensitive dye (indigo disulfonate, I2S)
- Reaction stoichiometry

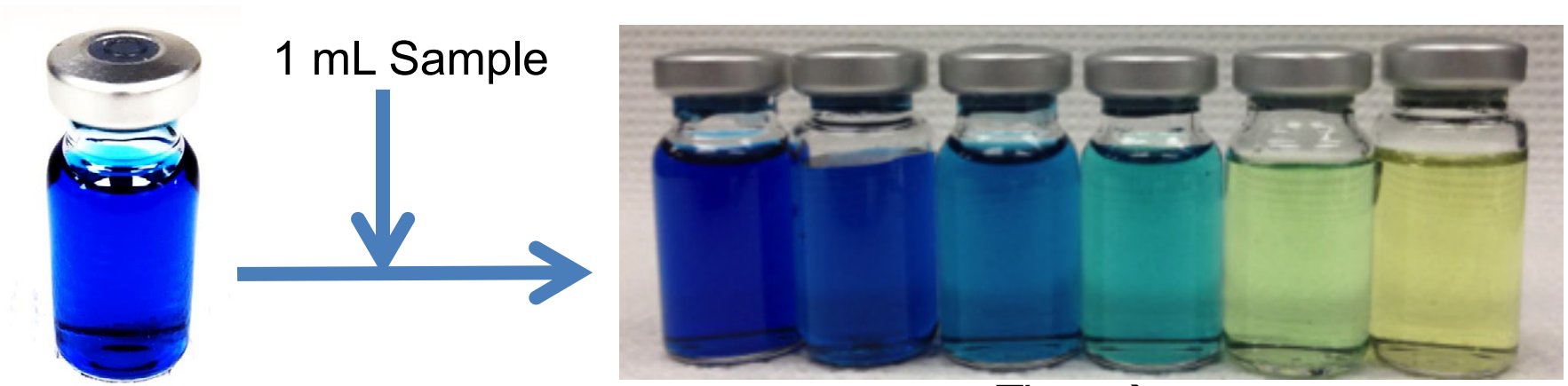
$$3I2S_{ox} + 2Fe^{0} + 6H^{+} \rightarrow 3I2S_{red} + 2Fe^{3+}$$

- 1.5 moles of I2S required to reduce 1 mole of nZVI
- Uses UV-vis spectrophotometry at 610 nm to quantify reduction



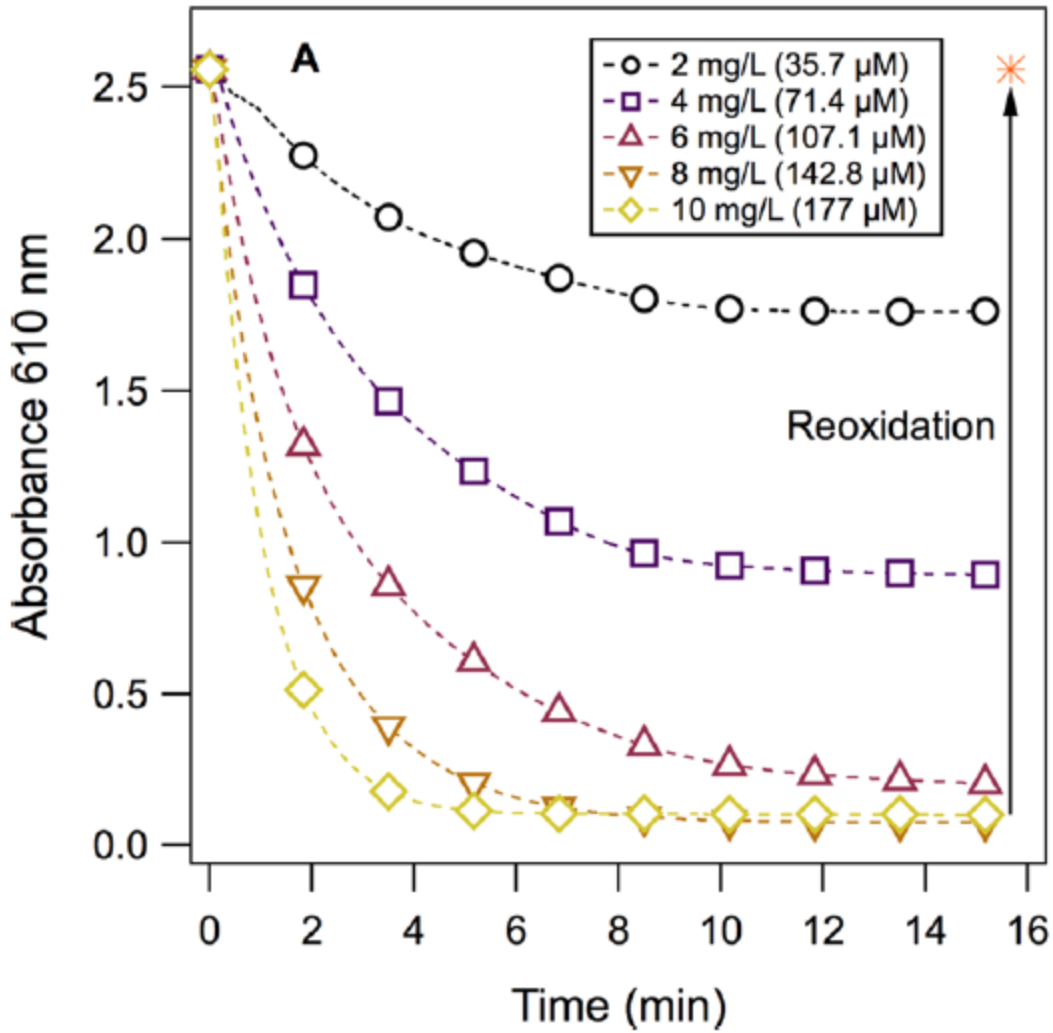
Measurement of nZVI in Water

- Vials contain 10 mL of O_2-free140 µM I2S
- 1 mL sample injected into vial
- Absorbance (610 nm) monitored over time

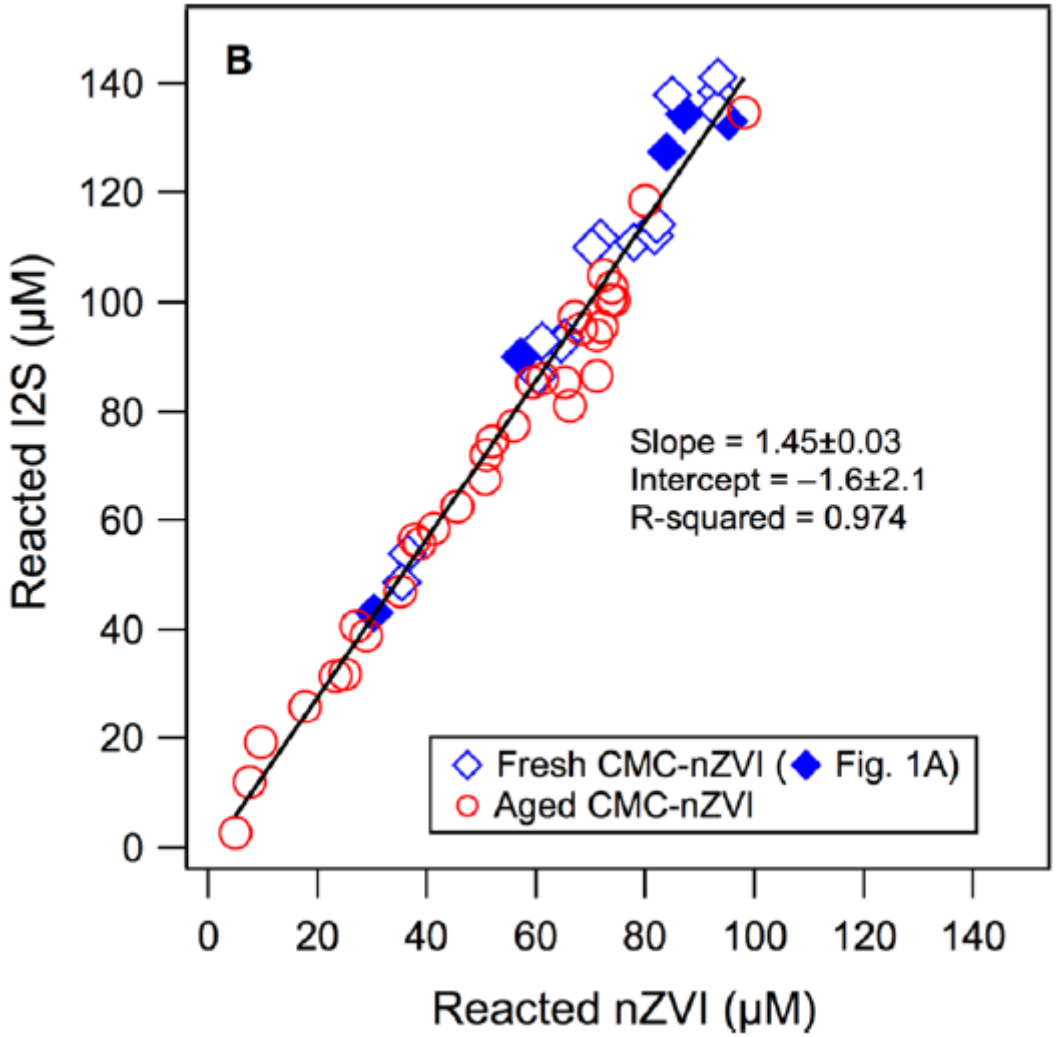


Time →

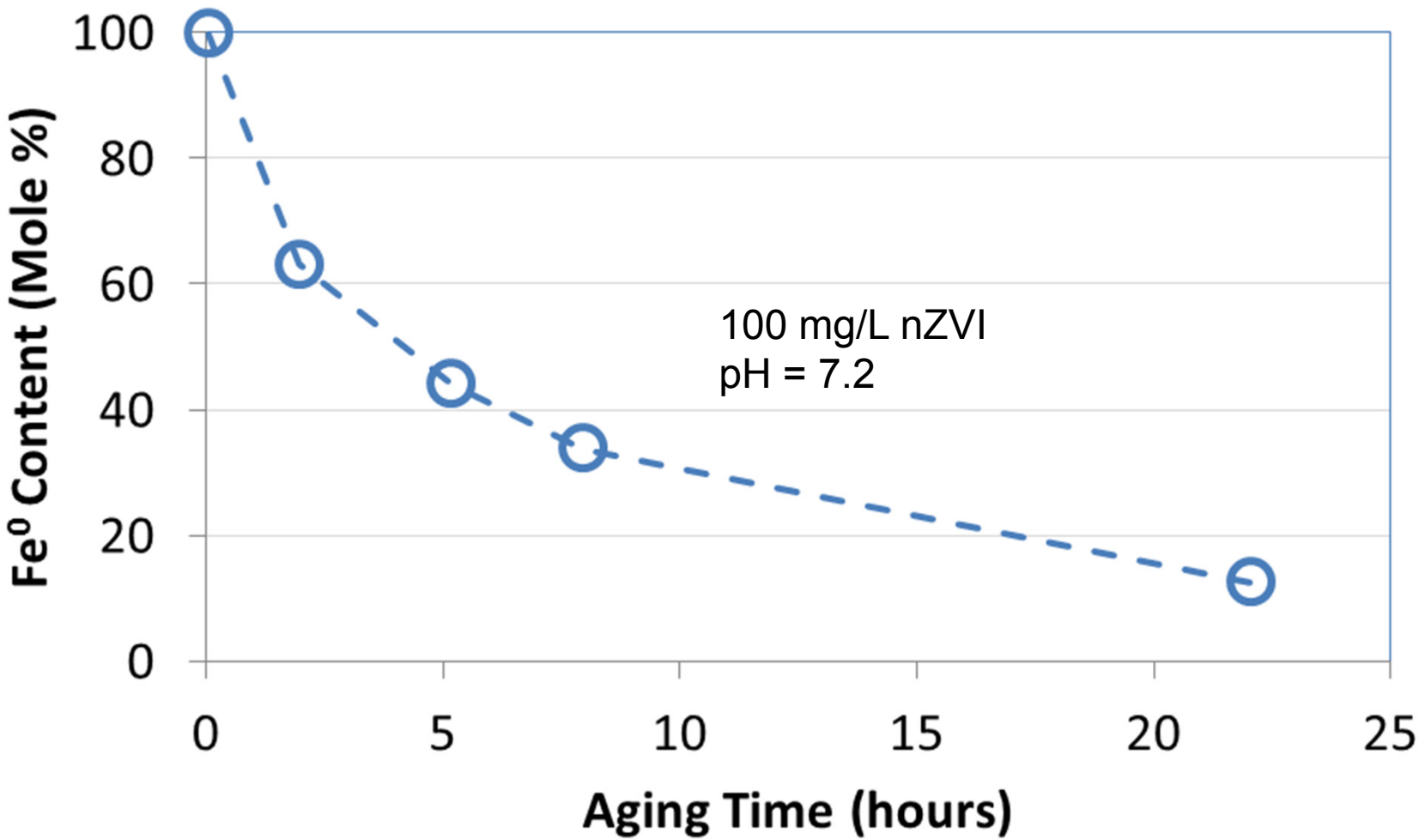
Reduction of I2S by nZVI



Estimate of Reaction Stoichiometry

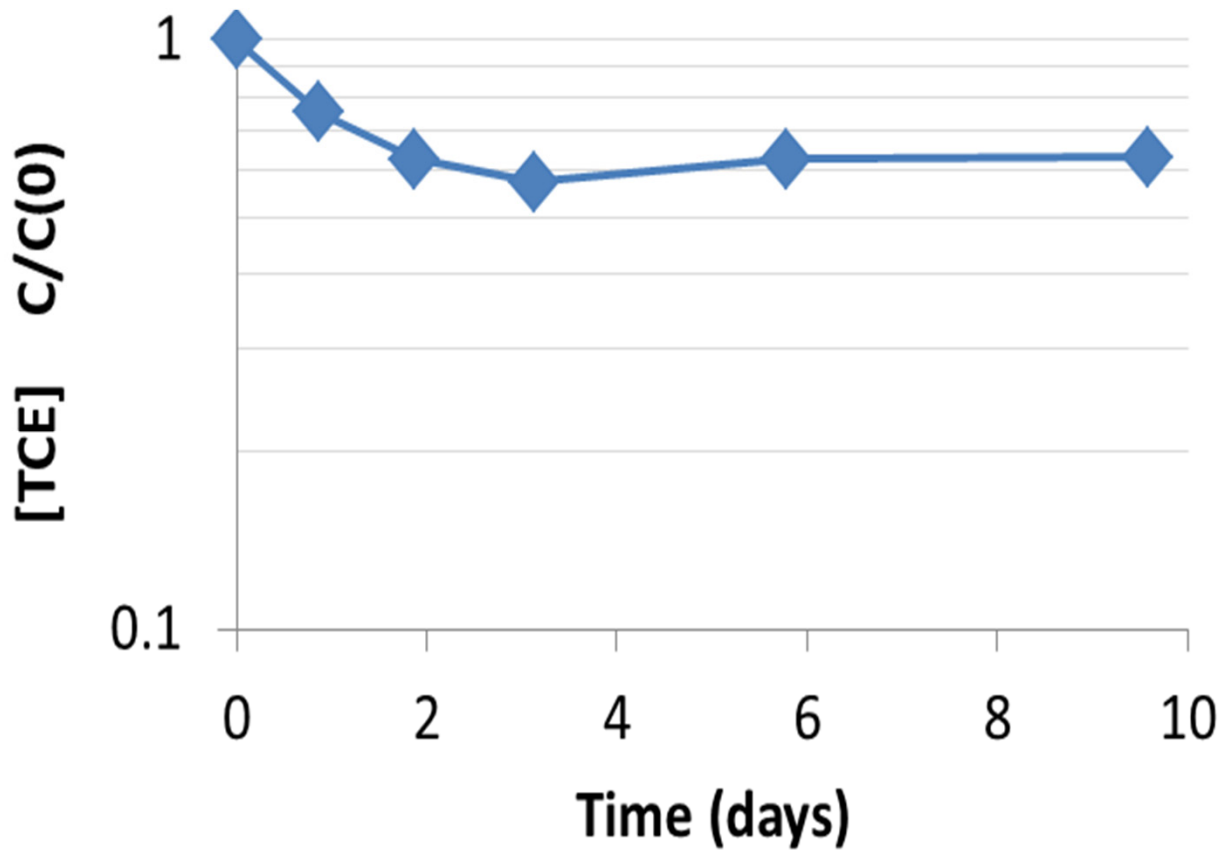


Lifetime of nZVI in Anoxic Water



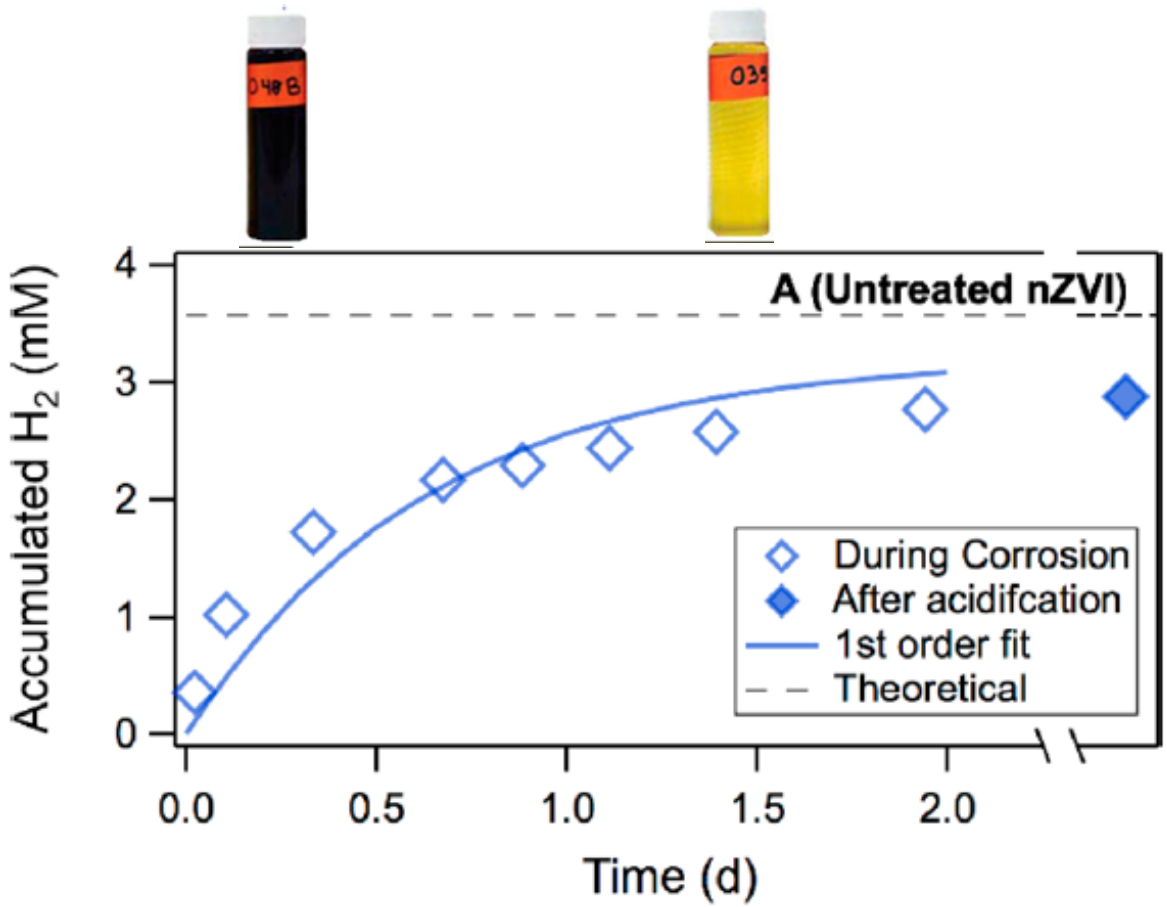
TCE Reduction by nZVI

$$C_2Cl_3H + 3Fe^0 + 3H^+ \rightarrow C_2H_4 + 3Fe^{2+} + 3Cl^-$$



H_2 from nZVI Reaction with Water

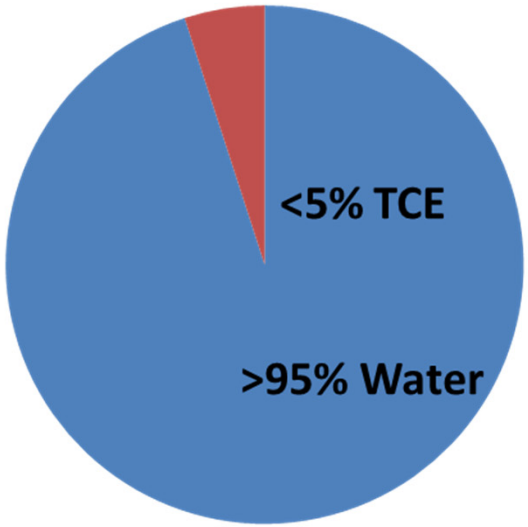
$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2(g)\uparrow$$



TCE Reduction by nZVI

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2(g)\uparrow$$

$$C_2Cl_3H + 3Fe^0 + 3H^+ \rightarrow C_2H_4 + 3Fe^{2+} + 3Cl^-$$



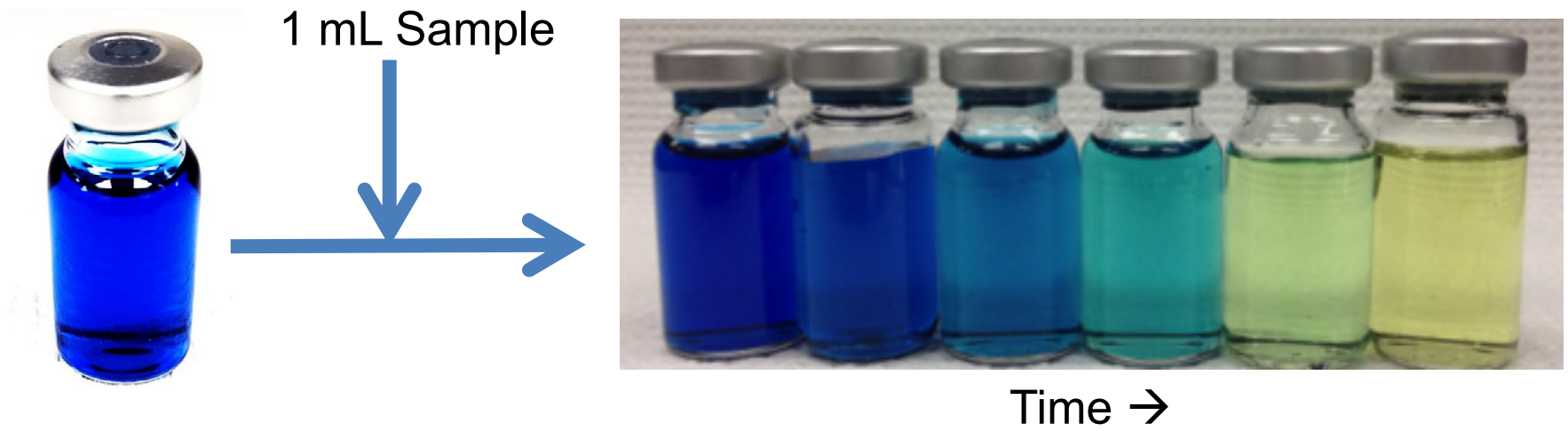
Percentages of nZVI reducing equivalents expended on TCE and water

nZVI Field Injection

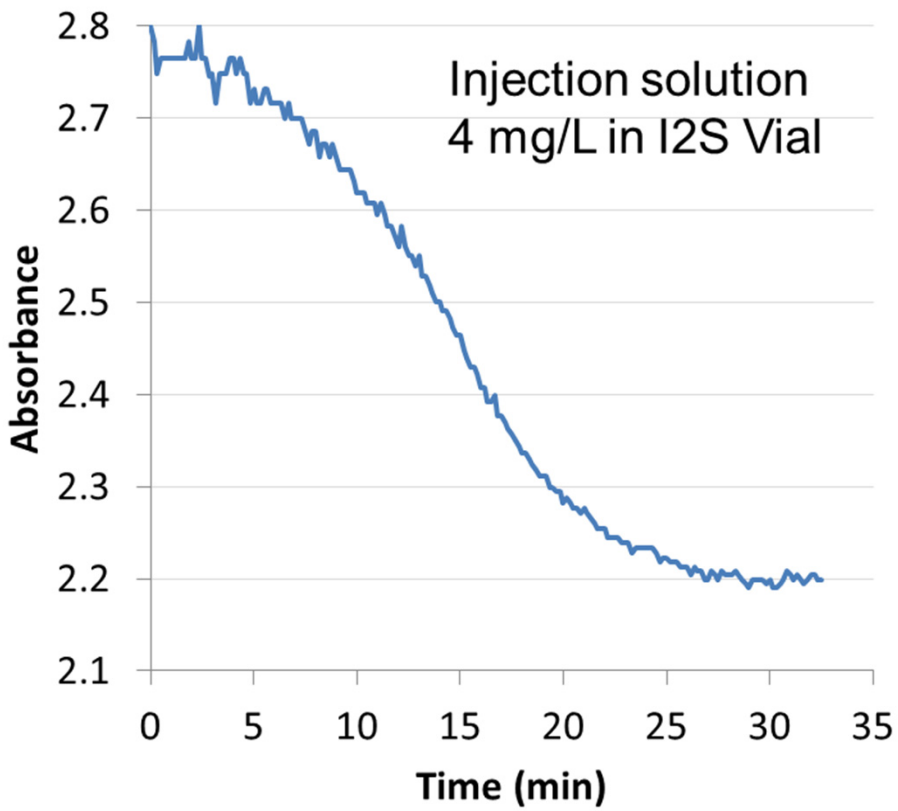
- Conducted by O'Carroll and colleagues at UWO
- CMC-nZVI w/ Dithionite
- Gravity feed, sandy aquifer
- OHSU/SERDP role was to assess reduction kinetics and capacity

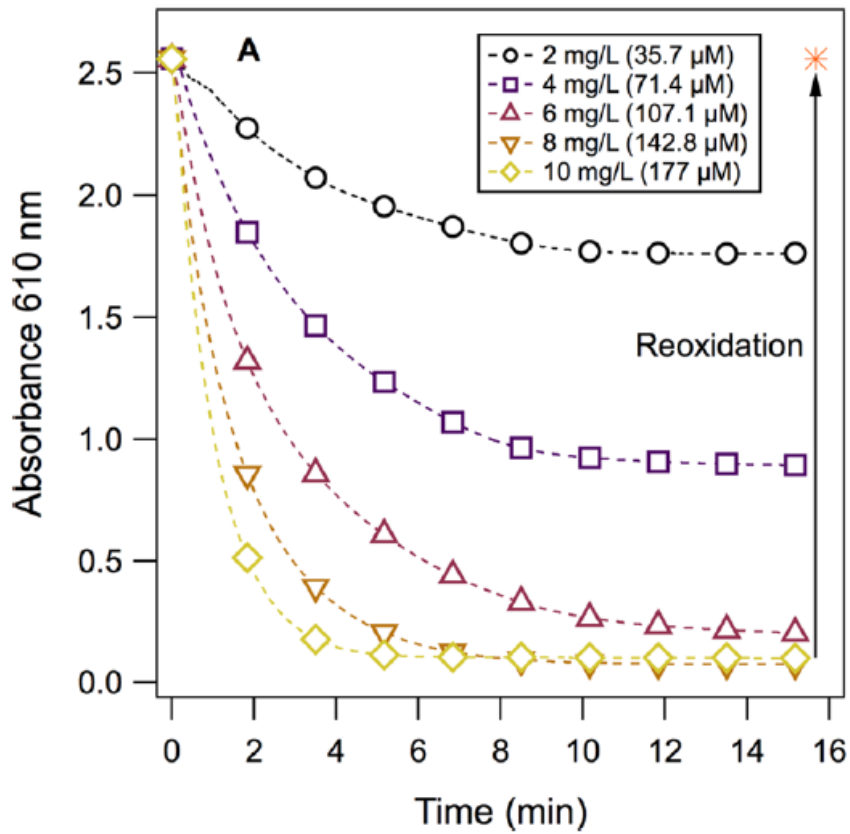
nZVI Field Injection

- Vials contain 10 mL of O_2-free140 µM I2S
- 1 mL sample injected into vial
- Absorbance (610 nm) monitored over time



Reduction of I2S by nZVI





I2S/nZVI Theoretical Stoichiometry

Fe(0) Reactions	Stoichiometry	# e- per Fe	Theor. Stoic.
Water	$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2(g)\uparrow$	2	1
I2S	$3I2S_{ox} + 2Fe^0 + 6H^+ \rightarrow 3I2S_{red} + 2Fe^{3+}$	3	**1.5**
Fe(II) Reactions			
Water	No water/FeS reaction	0	0
I2S	$I2S_{ox} + 2Fe^{2+}(solid) + 2H^+ \rightarrow I2S_{red} + 2Fe^{3+}(solid)$	1	**.5**

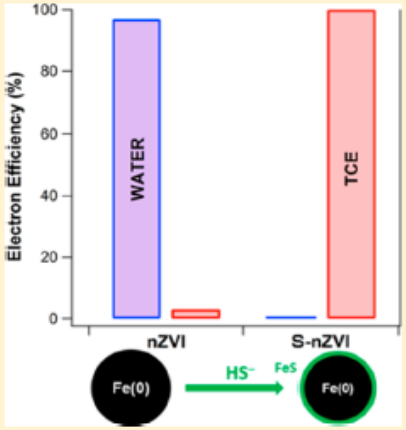
Assessing Sulfidated nZVI for ISCR

Sulfidation of Nano Zerovalent Iron (nZVI) for Improved Selectivity During In-Situ Chemical Reduction (ISCR)

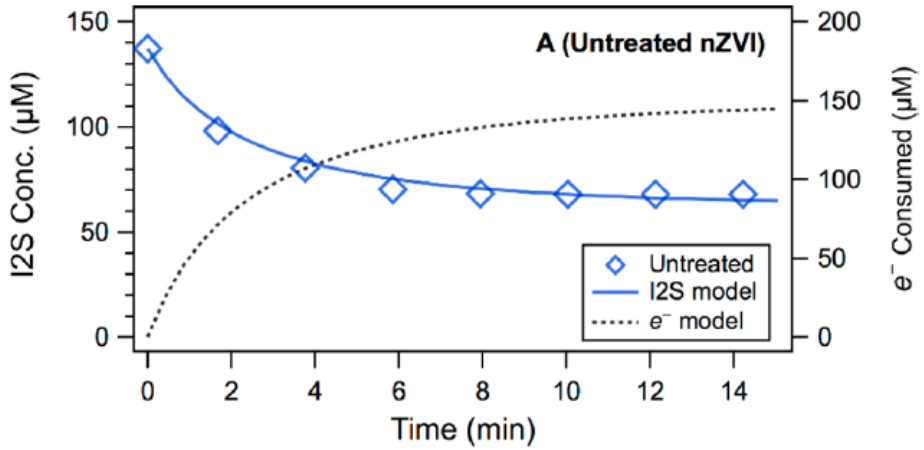
Dimin Fan,[†,§] Graham O'Brien Johnson,[†] Paul G. Tratnyek,[†] and Richard L. Johnson*[,†,‡]

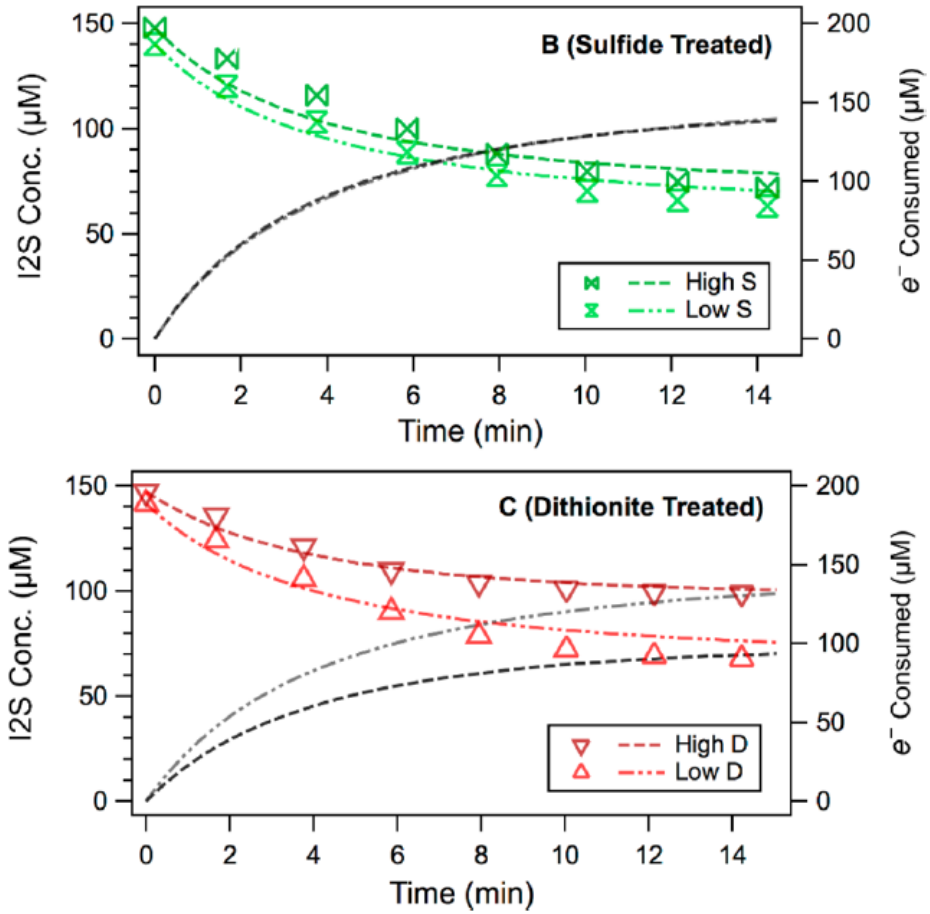
Environ. Sci. Technol. 2016, ASAP
DOI: 10.1021/acs.est.6b02170

ABSTRACT: The high reactivity of nano zerovalent iron (nZVI) leads to inefficient treatment due to competition with various natural reductant demand (NRD) processes, especially the reduction of water to hydrogen. Here we show that this limitation can be alleviated by sulfidation (i.e., modification by reducing sulfur compounds). nZVI synthesized on carboxylmethylcelluose (CMC-nZVI) was sulfidated with either sulfide or dithionite. The reactivity of the resulting materials was examined with three complementary assays: (i) direct measurement of hydrogen production, (ii) reduction of a colorimetric redox probe (indigo disulfonate, I2S), and (iii) dechlorination of trichloroethylene (TCE). The results indicate that sulfidation at S/Fe molar ratios of ≥0.3, effectively eliminates reaction with water, but retains significant reactivity with TCE. However, sulfidation with sulfide leaves most of the nZVI as Fe(0), whereas dithionite converts a majority of the nZVI to FeS (thus consuming much of the reducing capacity originally provided by the Fe(0)). Simplified numerical models show that the reduction kinetics of I2S and TCE are mainly dependent on the initial reducing equivalents and that the TCE reduction rate is affected by the aging of FeS. Overall, the results suggest that pretreatment of nZVI with reducing sulfur compounds could result in substantial improvement in nZVI selectivity.

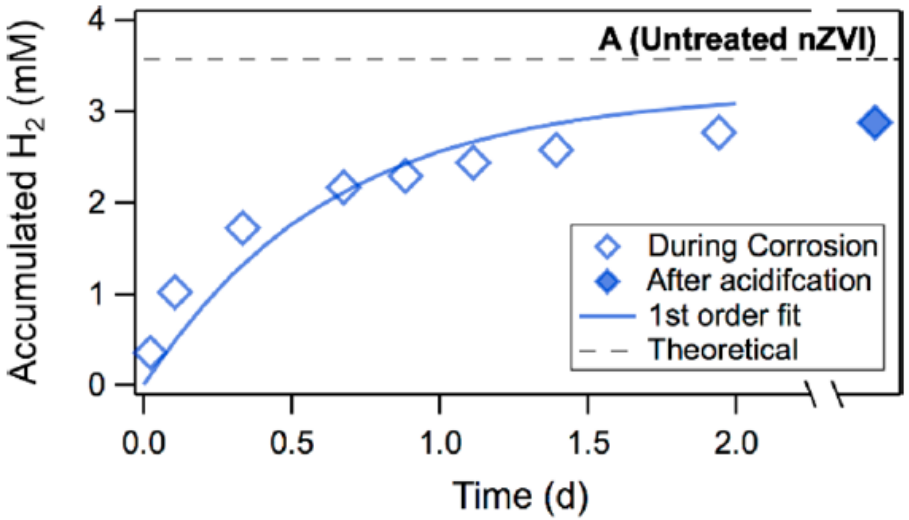


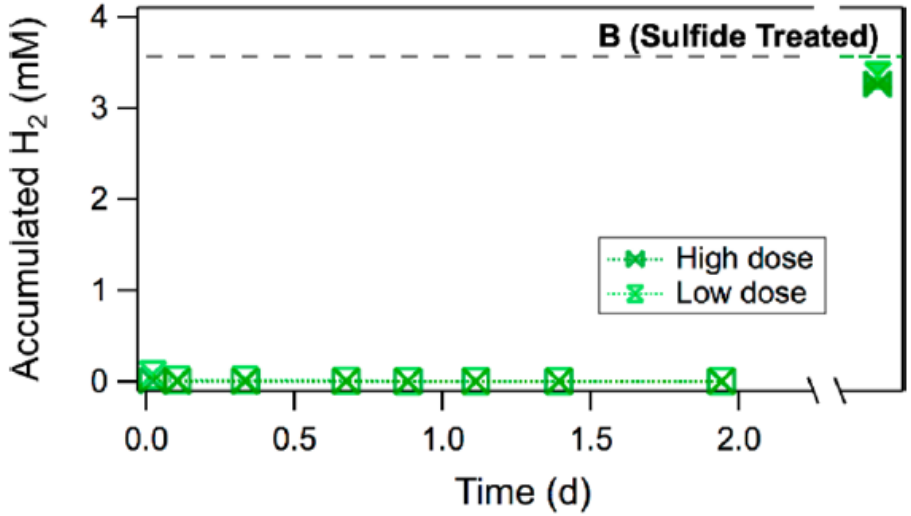
I2S Reduced by Sulfidated nZVI

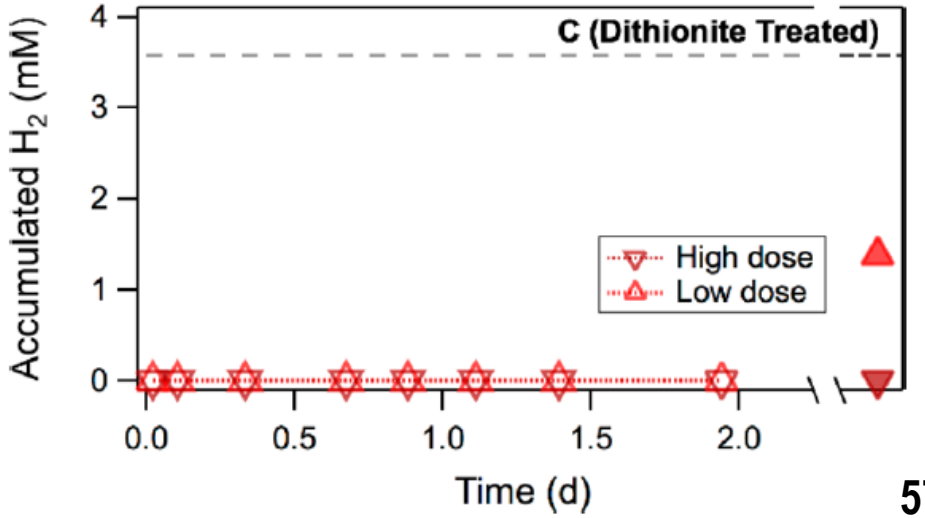




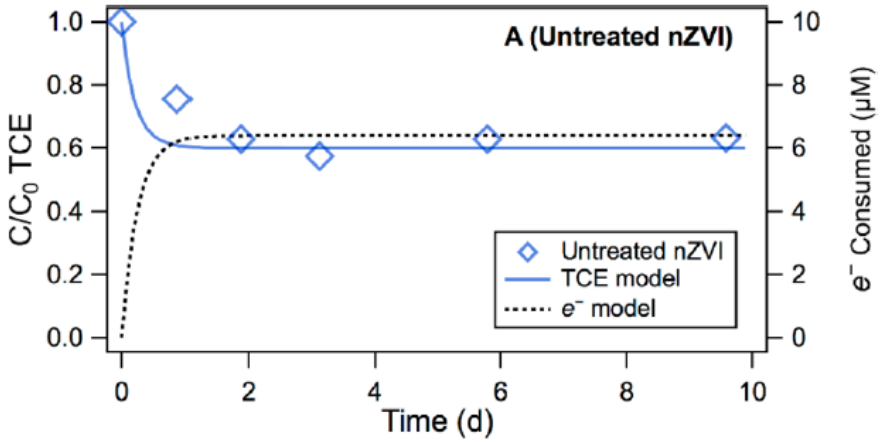
H_2 Evolution from Sulfidated nZVI

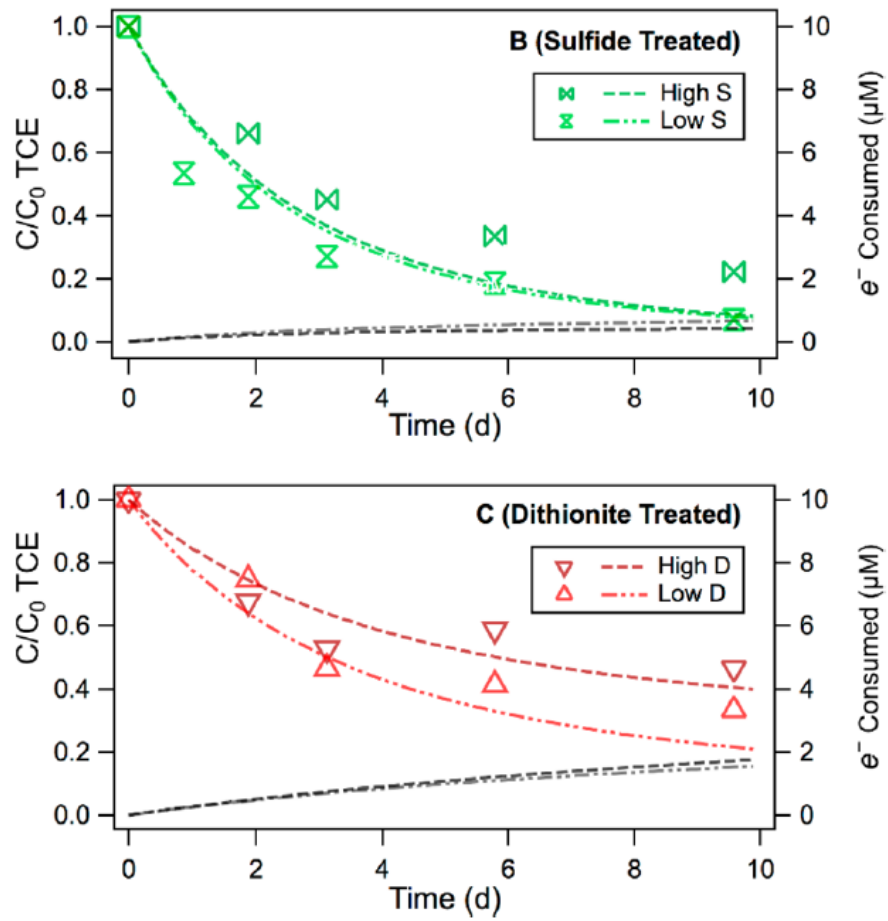




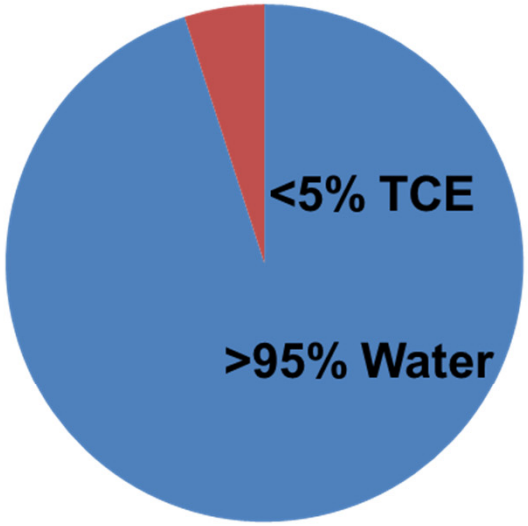


TCE Degraded by Sulfidated nZVI

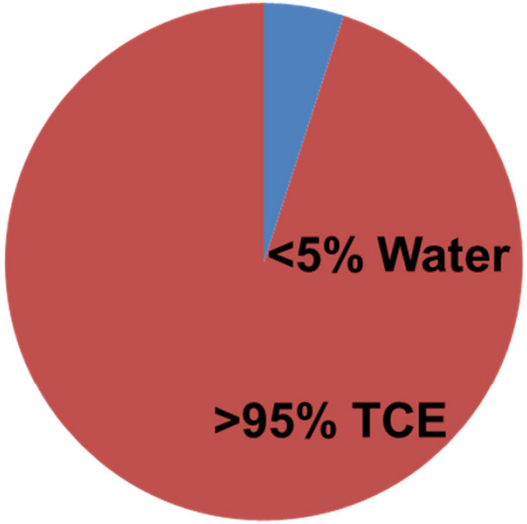




Reaction Efficiencies for nZVI



Untreated CMC/nZVI



CMC/nZVI sulfidated with S^{2-}

nZVI reducing equivalents expended on TCE and water

- CRPs were key for understanding this
- CRPs were readily field deployable

Key Points for Redox Assessment

1. Thermodynamic, kinetic and capacity are all important for assessing performance
2. CRPs provide rapid screening in field or lab
3. CRPs work for aqueous or solid phase
4. CRPs used to assess natural attenuation rates
5. CRPs used to assess range of engineered solutions (ISCR, ISCO)

Looking ahead (ER-2621)

1. Focus will be on mineral surfaces
2. Field samples will be collected using cryogenic core sampling
3. CRPs will be used to estimate kinetics of slow contaminant reactions
4. Focus on data needed to close sites (e.g., slow reactions in low-K zones)
5. Budget for drilling at 2-3 sites

For additional information, please visit

https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-2308

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Q&A Session 2

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The next webinar is on September 22, 2016

"Managing the Brown Treesnake Headache: Assessment of the Aerial Acetaminophen Bait Drop on Guam"

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Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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