PROTECT

Puerto Rico Testsite for Exploring Contamination Threats

NIEHS SRP P42 Research Program

The Potential for Solar-Powered Remediation

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Content

- Relevance
- Concept and Basics
- Example: Hexavalent Chromium Transformation
- Research Translation
- Current Effort
- Summary and Acknowledgment

RELEVANCE

http://www.clu-in.org/greenremediation/

EPA's strategic plan strives for cleanup programs that *use natural resources and energy efficiently*, *reduce negative impacts on the environment*, minimize pollution at its source, and reduce waste to the greatest extent possible.

Solar Energy use at Superfund Sites: Examples

- Aerojet-General Corporation CA, Trichlorothene (TCE) and perchlorate: Use solar energy to partially meet power requirements for pump-and-treat system.
- Apache Powder AZ, heavy metals and explosives: constructed wetland system. Used a solar-powered centrifugal pump to promote water recirculation in the wetlands system.
- Crozet Orchard VA, metals and pesticides: phytoremediation. Uses solar-powered low-flow pumps to transfer water from a hill-bottom spring to a second storage tank.
- Delfasco Forge TX, TCE vapor. Use solar energy to power exhaust systems addressing TCE vapor intrusion.

EPA's Relevant Activities

- Emphasize the use of renewable energy for cleanup operations
- Developed BMP's on clean fuels and emission technologies
- Evaluating tools for calculating environmental "footprints" of cleanup
- *EPA's 2011-2015 Strategic Plan includes continued work to reduce the energy use and environmental footprint during site investigation and remediation*

Research Needs/Opportunities:

Sustainable Solar-Powered "Active" Remediation

CONCEPT AND BASICS

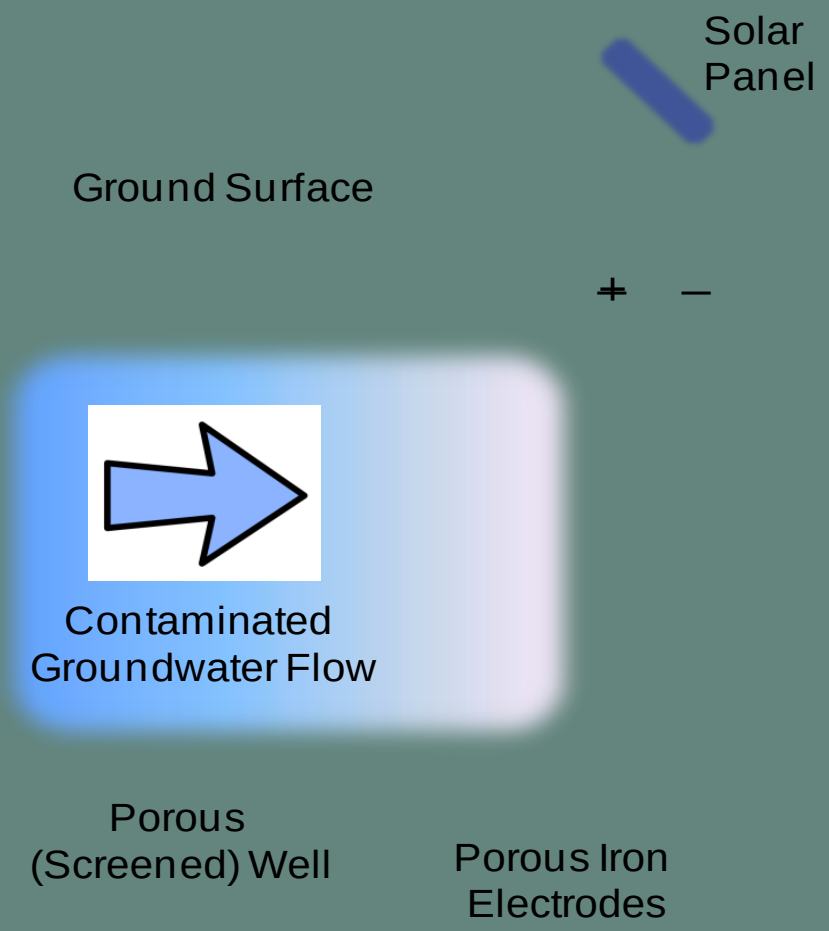
Background

- In many cases, remediation is based on redox manipulation of groundwater for transformation and/or immobilization of contaminants
- Redox manipulation is usually achieved by injection of additives that are oxidizing or reducing; e.g., HRC, ORC, ferrous sulfate, ZVI
- Transformation occurs by chemical and/or biological processes
- Challenges: Efficiency; Sustainability; Delivery; Cost

Solar-Powered Remediation – Concept –

- Adopt electrolysis to manipulate and control groundwater redox conditions for chemical and/or biological transformation of contaminants
- Use solar panels for electric power required for electrolysis
- Treatment systems could include well injections or permeable reactive barrier systems
- Potential target contaminants:
  - Chromium, Arsenic, Chlorinated solvents, PAH's, others

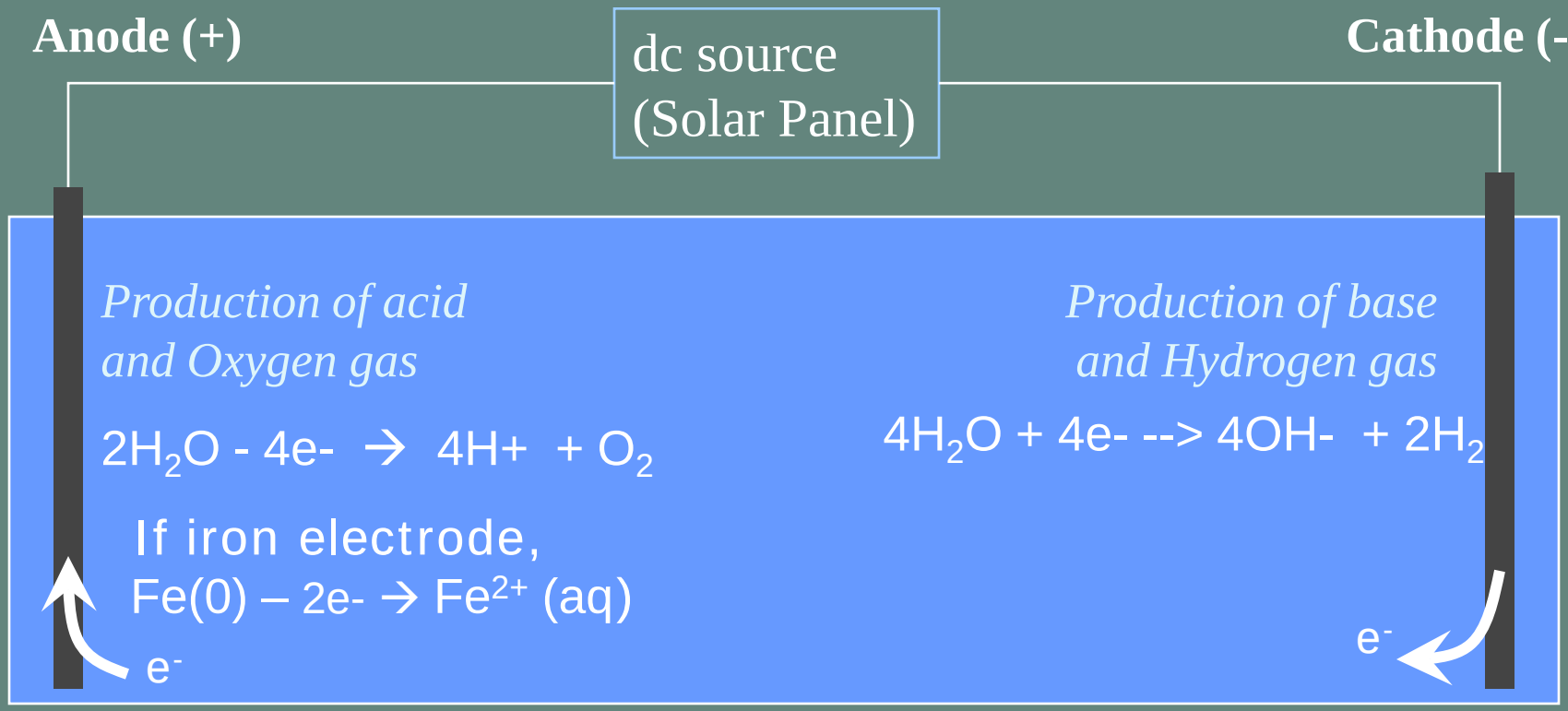
Solar-Powered Remediation – Concept –



Renewable energy for "sustained" manipulation of groundwater redox conditions

Basics: Electrolysis

Charge/Mass transfer at the electrodes (Faraday's Law)



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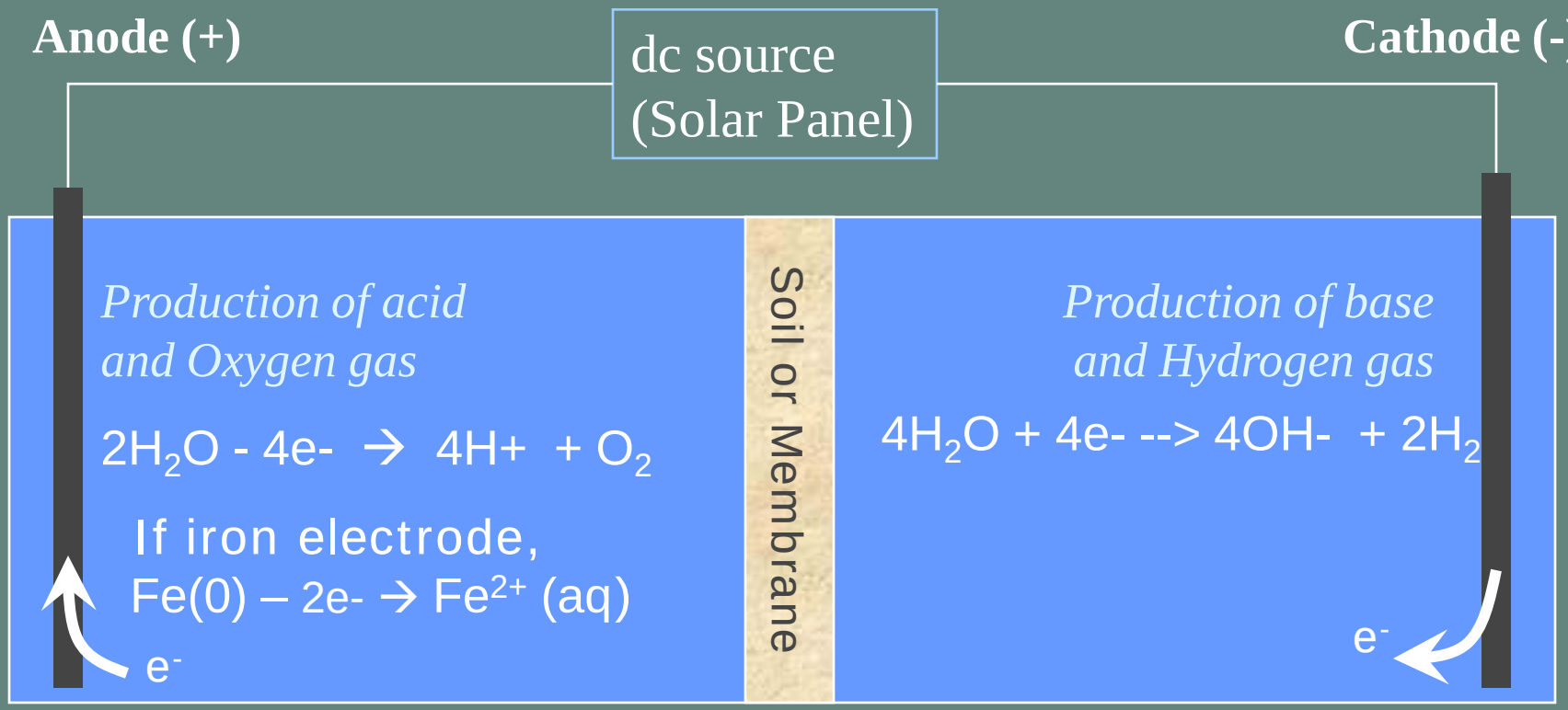


Example Strategy 1 – O_2/H_2 Production –

- $H_2O \rightarrow ½\ O_2 + 2H^+ + 2e-$ (Anode)
- $2H_2O + 2e- \rightarrow 2OH- + H_2$ (Cathode)
- Net reaction in a mixed electrolyte
  - $H_2O \rightarrow ½\ O_2 + H_2$
- Options:
  - Collect O_2 at the anode and allow H_2 to mix with GW
  - Collect H_2 at the cathode and allow O_2 to mix with GW

Example Strategy 2 – Fe Anode Redox –

- Iron Anode: $Fe(0) \rightarrow 2e^- + Fe^{2+}$ (aq)
- Sustainable generation and delivery of Fe(II) to GW
- Chemically reducing conditions develop
- Could be used in a mixed or isolated electrode reactor

Transformation Mechanisms

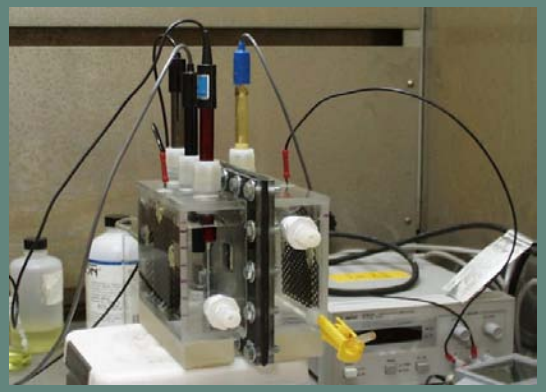
- Biological
  - Aerobic: by production of O_2 as an electron acceptor; e.g. PAH
  - Anaerobic: by production of H_2 as an electron donor; e.g. PCE
- Chemical
  - Reduction of hexavalent chromium
  - Oxidation of PAH and BTEX
  - Alkaline Hydrolysis: transformation of RDX
- Electrochemical
  - Direct oxidation at the anode or reduction at the cathode

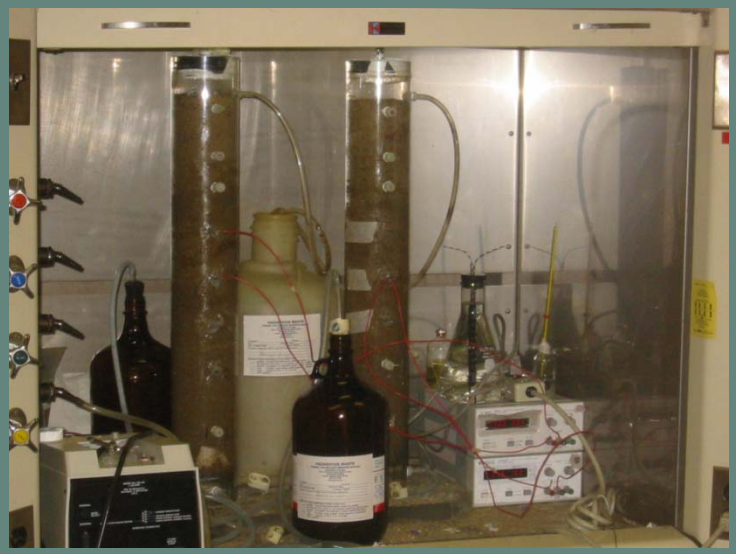
EXAMPLE – HEXAVALENT CHROMIUM

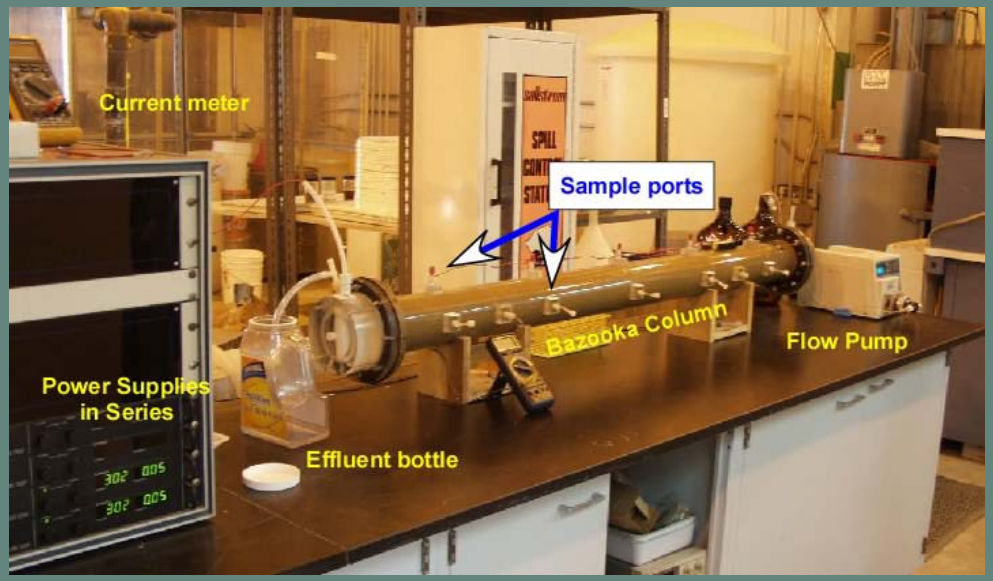
Laboratory Study:
Cr(VI) Reduction by Fe electrolysis

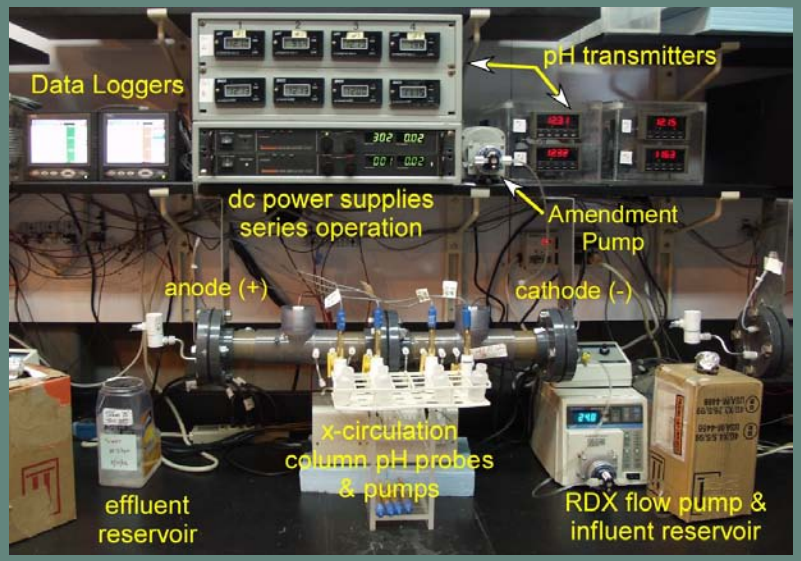
- Hypothesis:
  - Electrolysis using iron electrodes (anodes and cathodes) will induce Fe(II) (and H_2) dominated reducing conditions that can be manipulated for chemical reduction of Cr(IV).
- Justification:
  - The reactivity is similar to reduction by ZVI (single electrode redox)
- Advantages:
  - The kinetics of electrolysis and consequent redox and transformation can be controlled to optimize (accelerate or limit) the release of Fe(II)/H_2 by controlling the electric current density and polarity in a 2 electrode system.

Experimental Setup

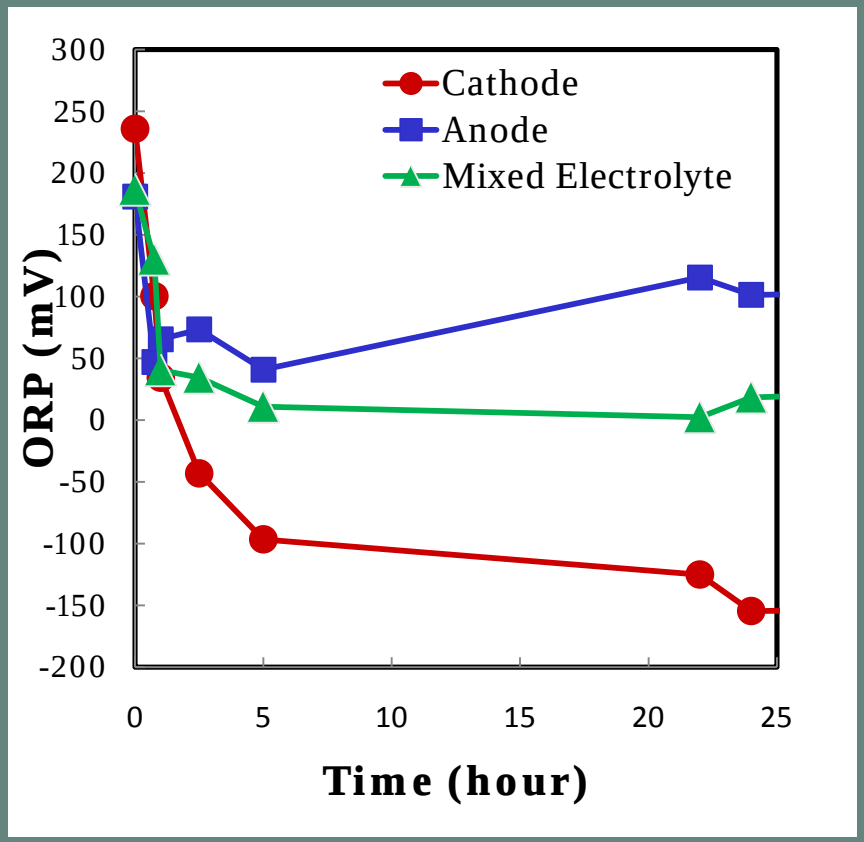


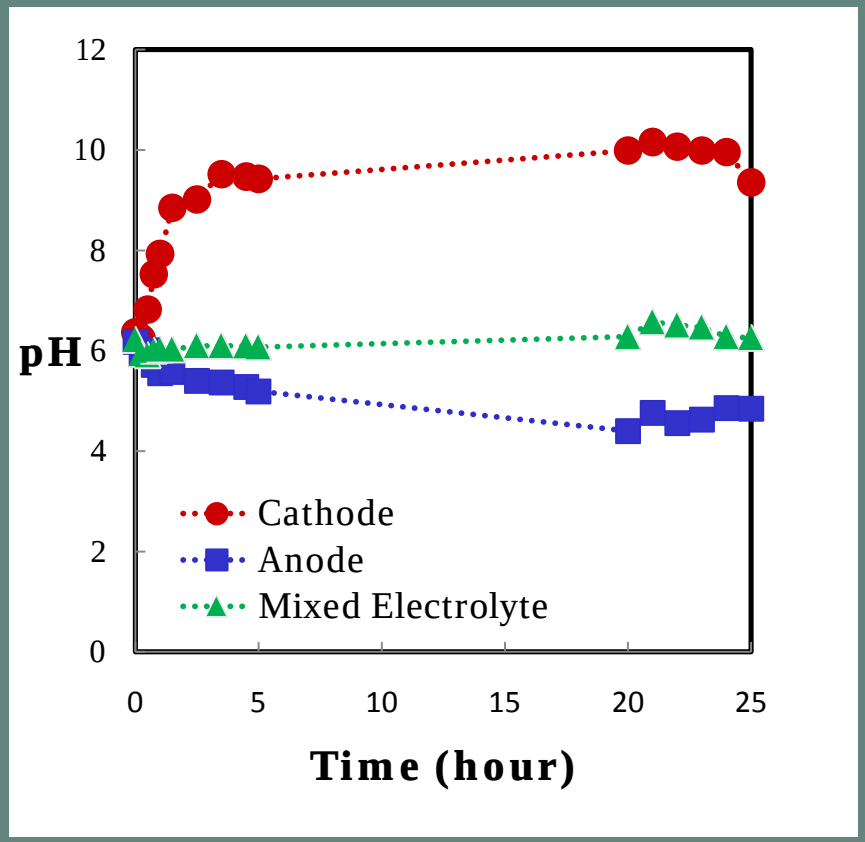






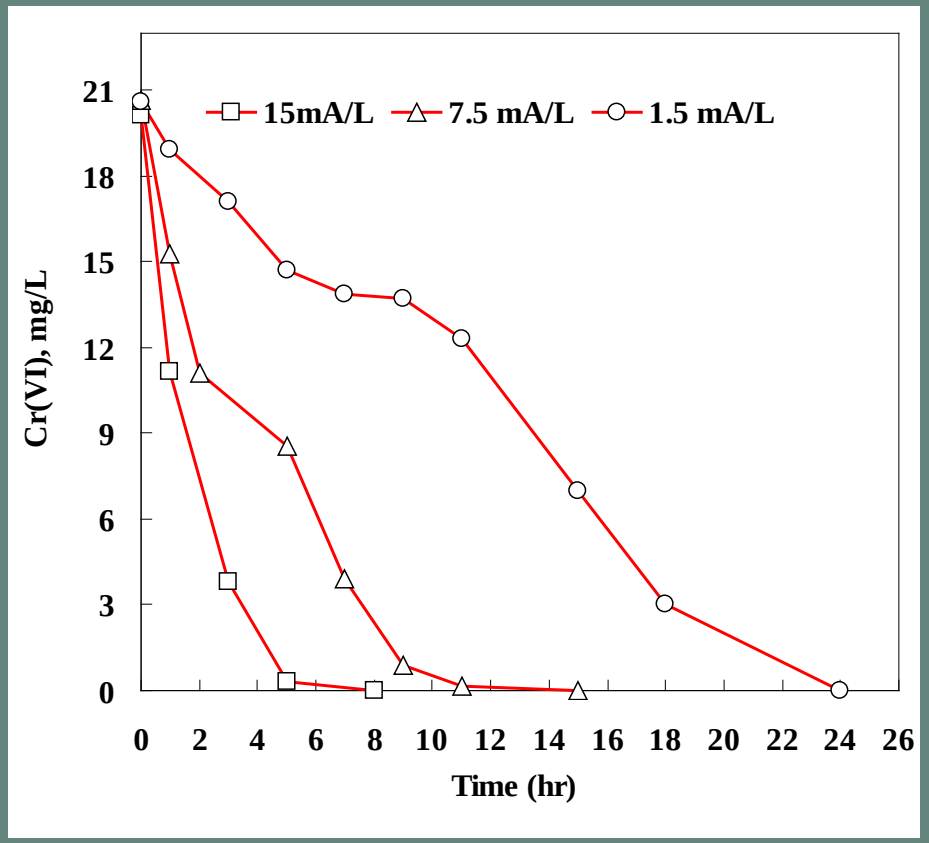
Results
– Batch Samples –

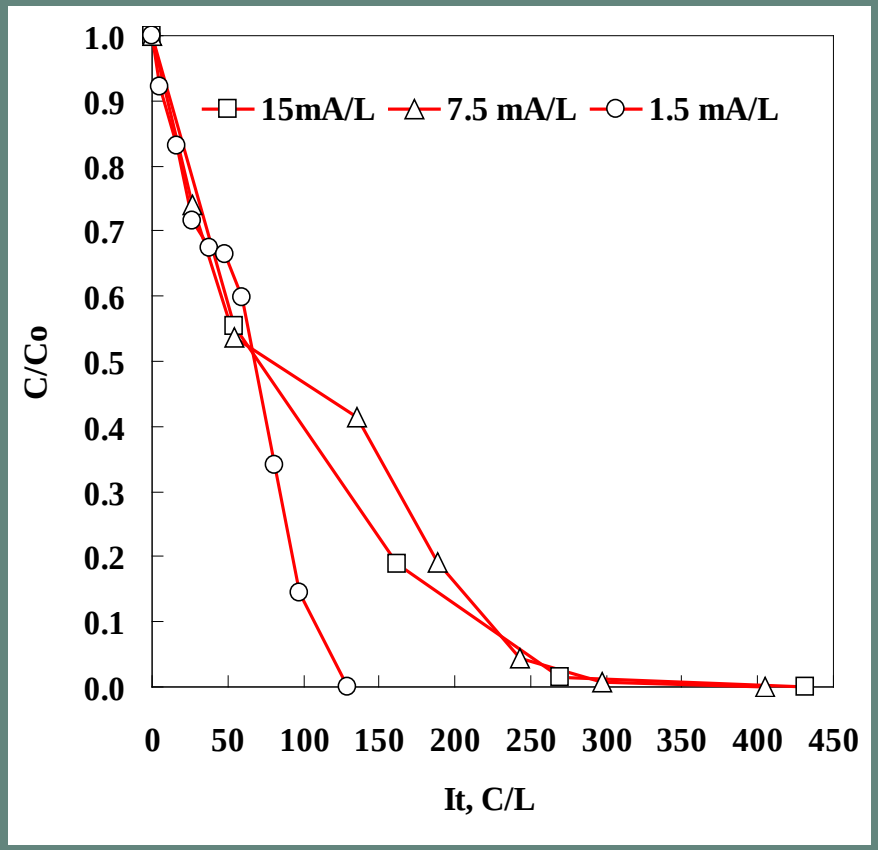




ORP and pH measurements under 1 mA/L using Fe electrodes for cases with separate and mixed electrolytes. Total voltage was on the order of 2 V in the separated and 0.5 V in the mixed electrolytes.

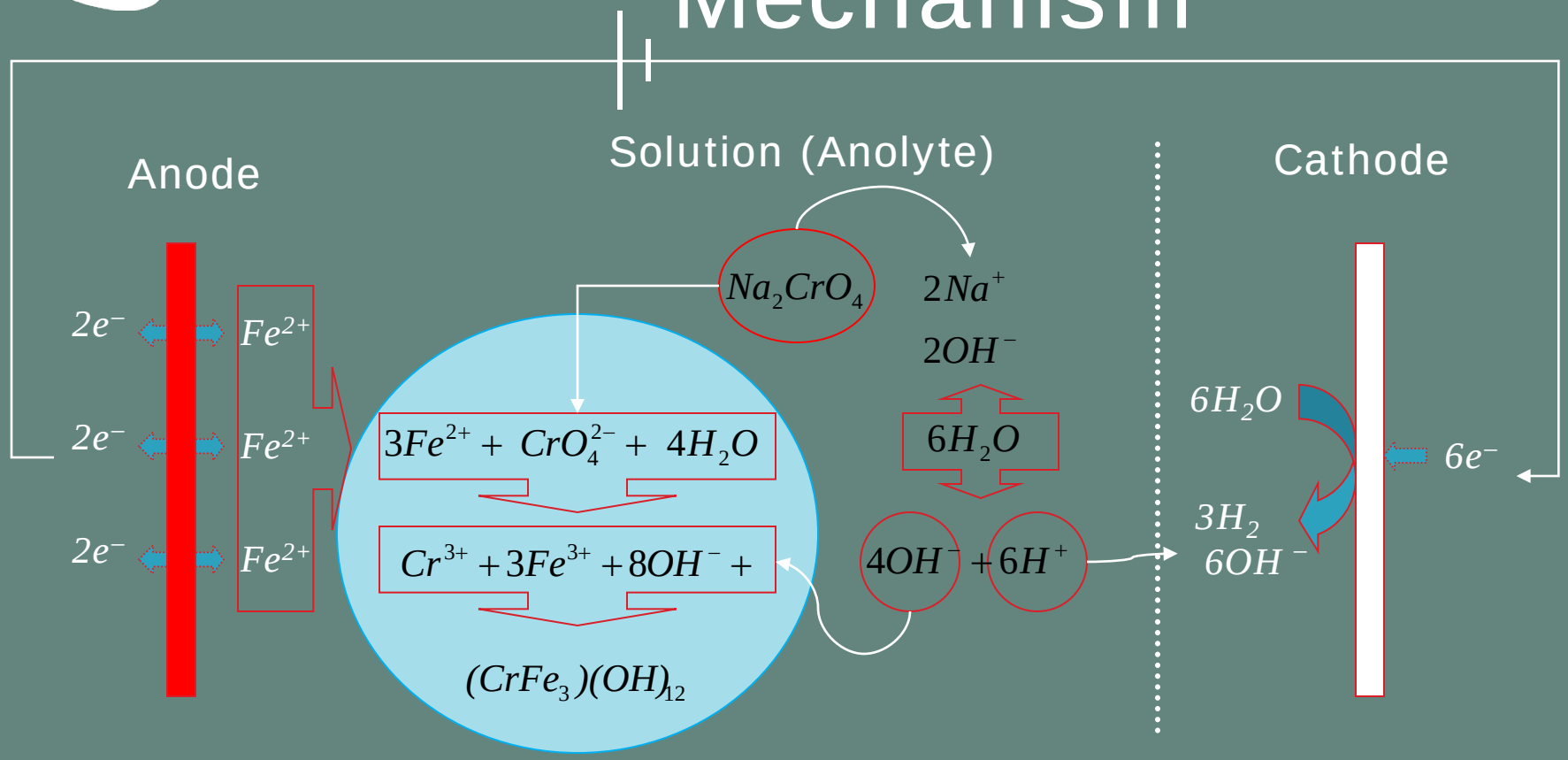
Results
– Batch Samples –





Initial Concentration = 20 mg/L

Cr(VI) Transformation Mechanism

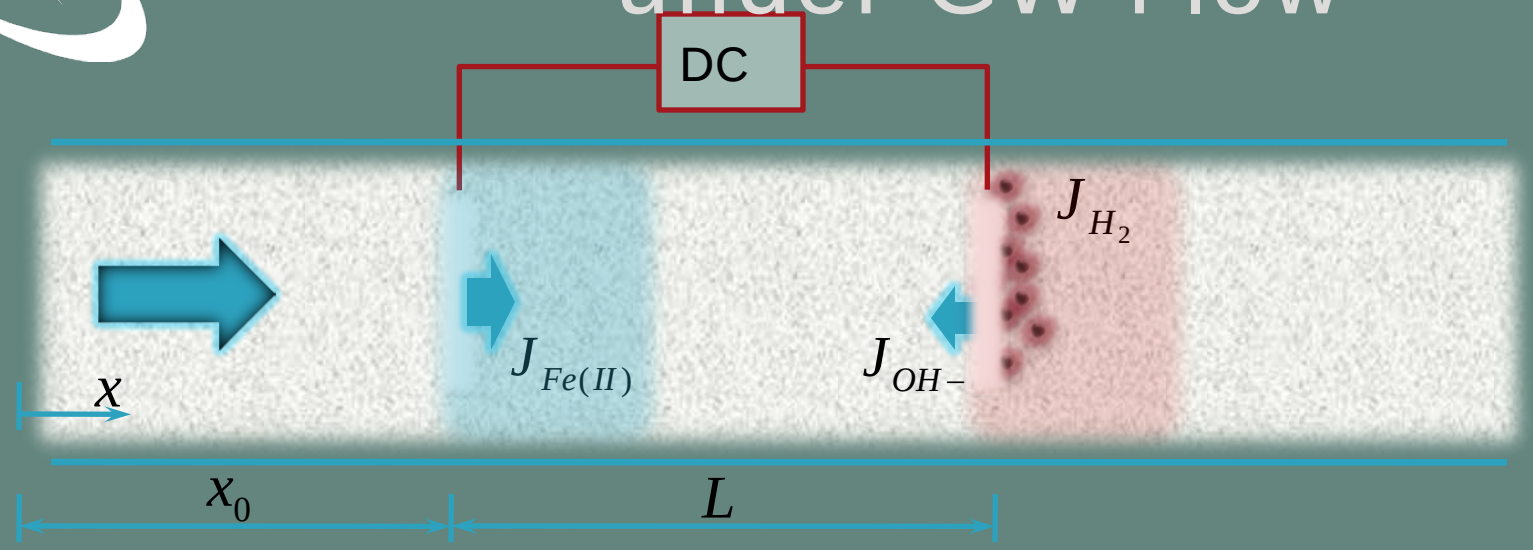


$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$

$$3Fe^{2+} + CrO_4^{2-} + 4H_2O \rightarrow Cr^{3+} + 3Fe^{3+} + 8OH^-$$

$$xCr^{3+} + (1\text{-}x)Fe^{3+} + 3OH^- \rightarrow (Cr_xFe_{1-x})(OH)_3$$

Electrochemical Redox under GW Flow



$$\frac{\partial nc_i}{\partial t} = nD\frac{\partial^2 c_i}{\partial x^2} - v\frac{\partial c_i}{\partial x} + nR_i$$

when $\quad \mathrm{i} = \mathrm{Fe(II)}$

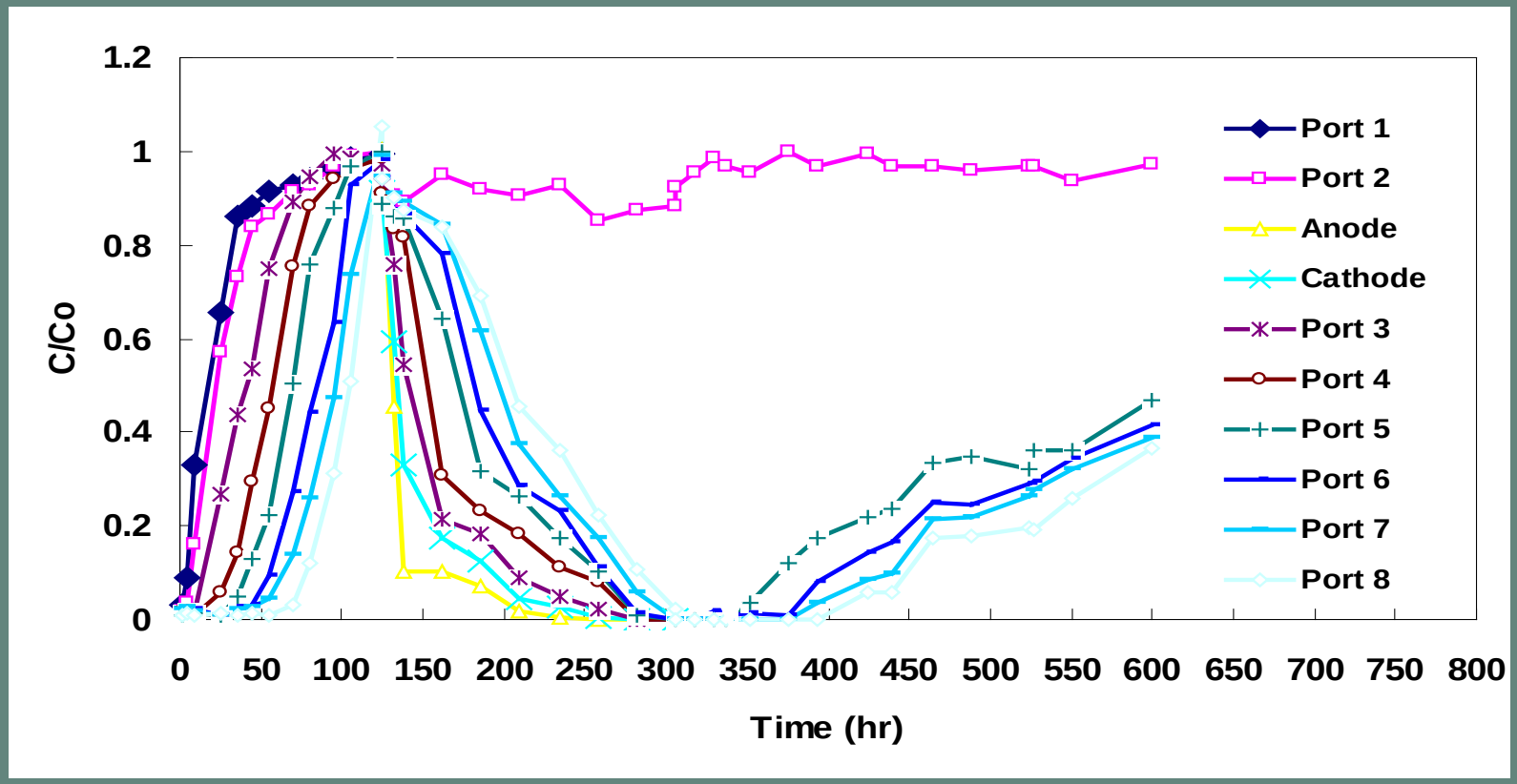
$$R_{Fe(II)} = \delta(x - x_0)J^e_{Fe(II)} + \left(\frac{\partial c_{Fe(II)}}{\partial t}\right)_{geochemistry}$$

when $\quad \mathrm{i} = \mathrm{OH-}$

$$R_{OH-} = \delta(x - x_0 - L)J^{\mathrm{e}}_{OH-} + \left(\frac{\partial c_{OH-}}{\partial t}\right)_{geochemistry}$$

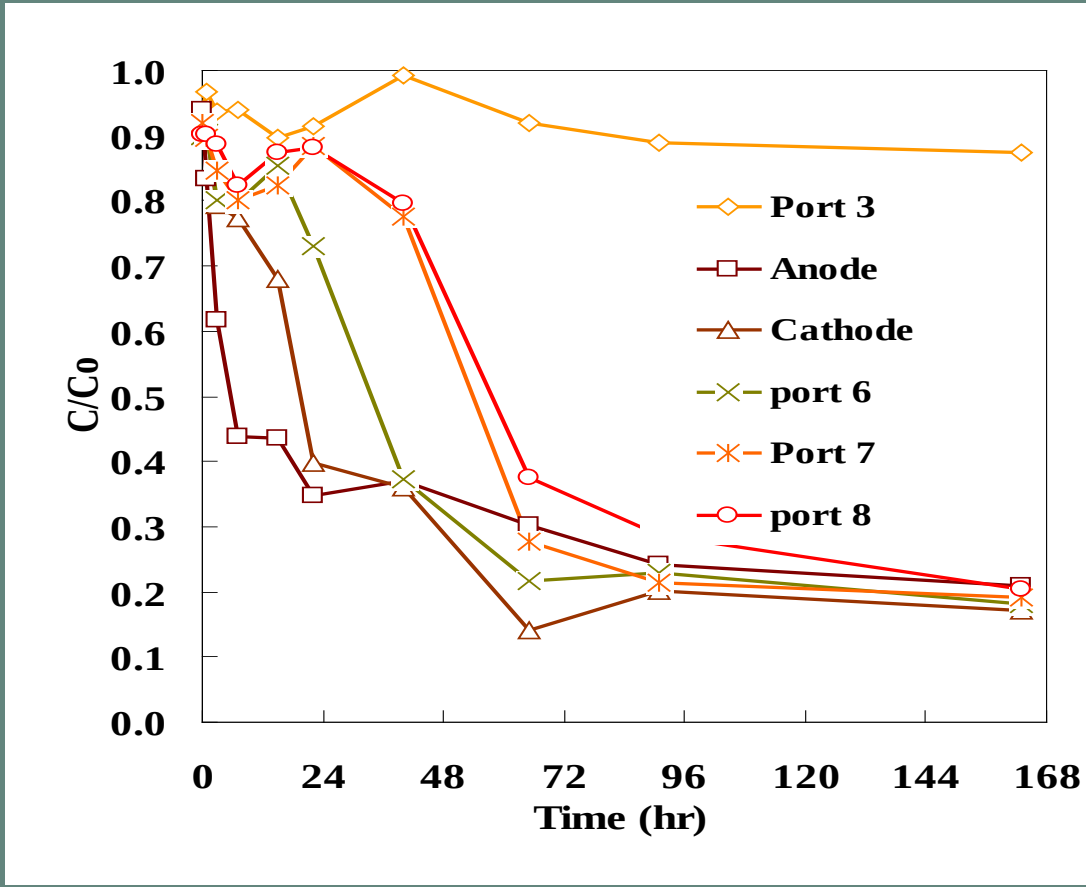
Cr Redox under Flow – Sand Column Tests –

Current density of 0.12A/m^2 ,
Electrode spacing of 2.5 cm



8 cm spacing showed similar results

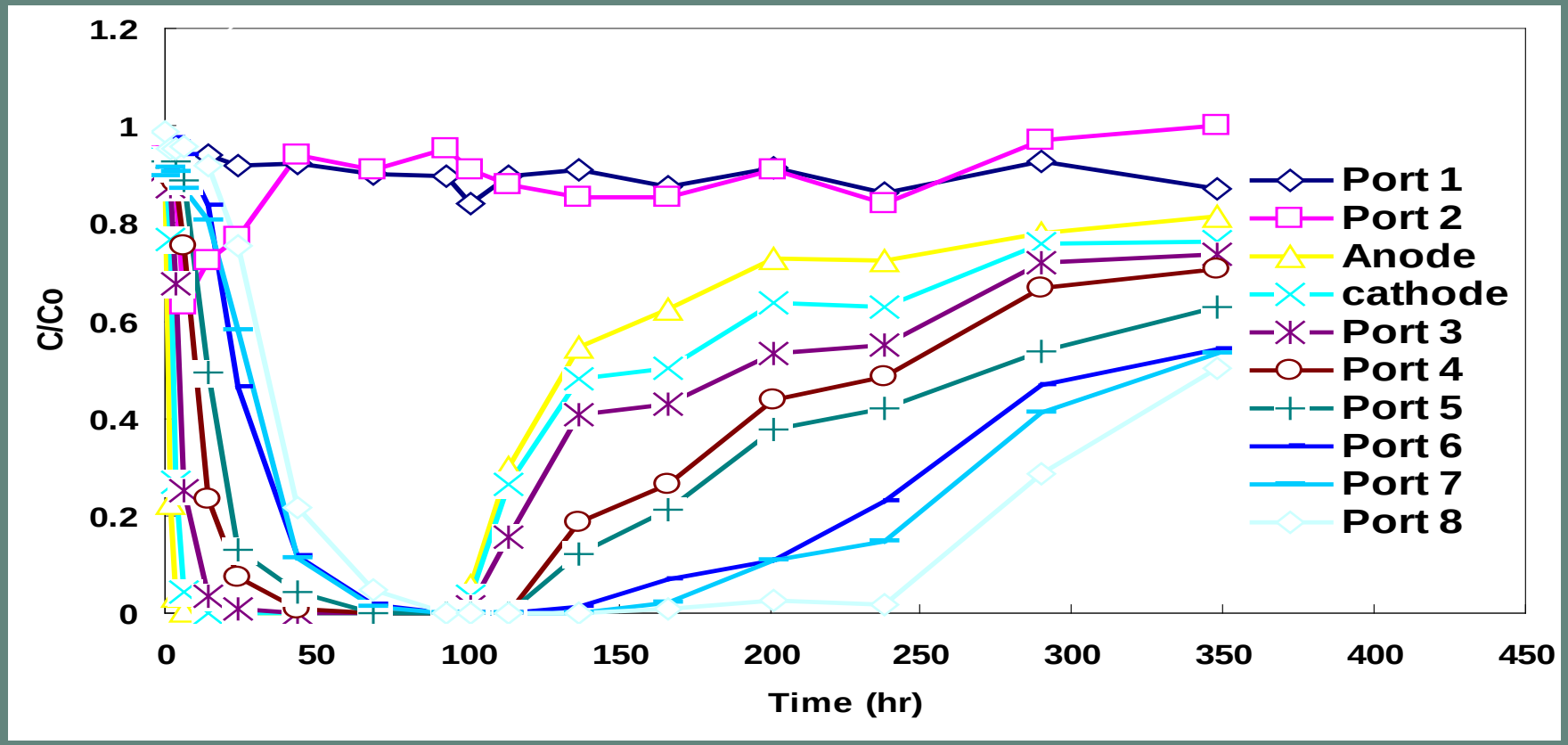
Cr Redox under Flow – Sand Column Tests –



Effect of Increasing flow rate – Current density of 0.12A/m²

Cr Redox under Flow – Sand Column Tests –

Current density of 0.36A/m^2
Electrode spacing of 2.5 cm



RESEARCH TRANSLATION

Practical Issues:
How Much Energy - Example?

- Assume average groundwater flow rate = 10 cm/day.
- Assume Average chromium concentration = 5 mg/l,
- Cr flux = 0.5 g/m^2.day or 0.01 mole/m^2.day.
- Required Fe(II) flux [$J_{Fe(II)}$] = 0.03 mole/m^2.day
- Required electric current density ($I=2J_{Fe(II)}F/0.75$) = 0.09 A/m^2.
- 50W solar panel (few $100) with 3 Amps (20 Volt) would cover a cross sectional area of more than 30 m^2 of flowing groundwater.

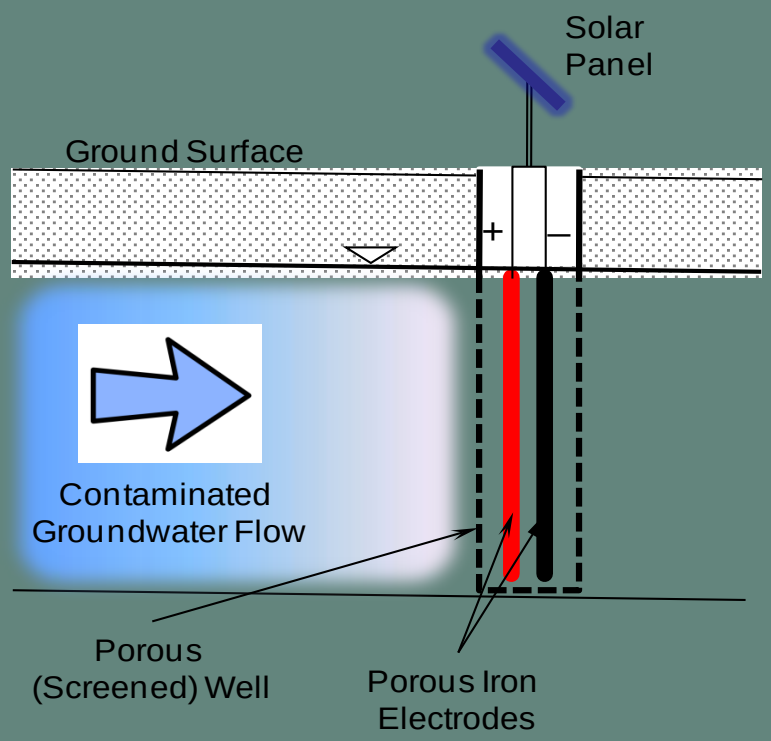
- Assumptions:
  - 3 moles of Fe(II) are required per 1 mole of Cr(VI).
  - 75% electrolysis efficiency

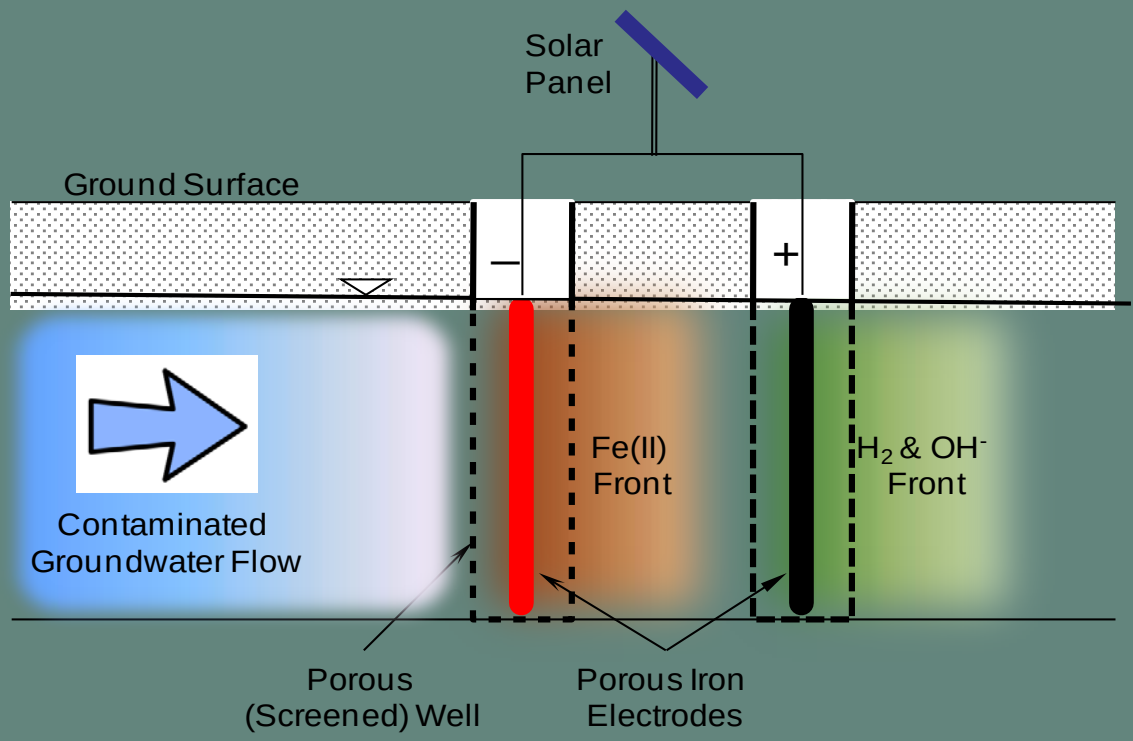
Potential Challenges

- Precipitation and changes in hydraulic conductivity
  - Function of electric current/flow rate, GW chemistry
- Passivation:
  - Less likely, but use polarity reversal if it occurs
- pH changes in GW
  - Function of electric current/flow rate, GW chemistry
- Delivery to contaminated zones

Process design is critical

Implementation Strategies – Examples –





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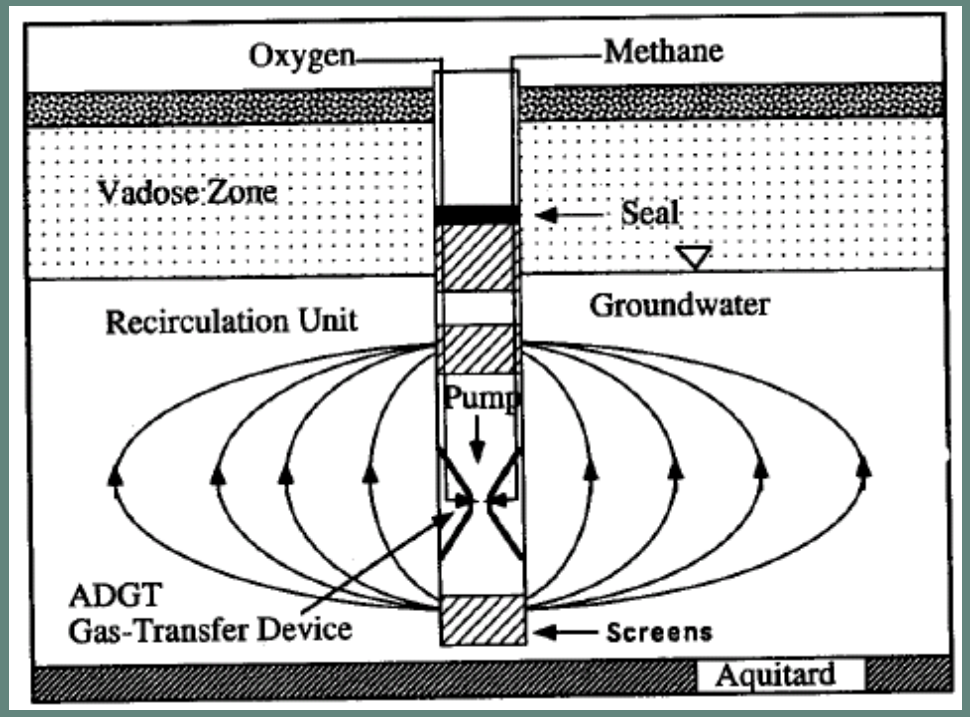
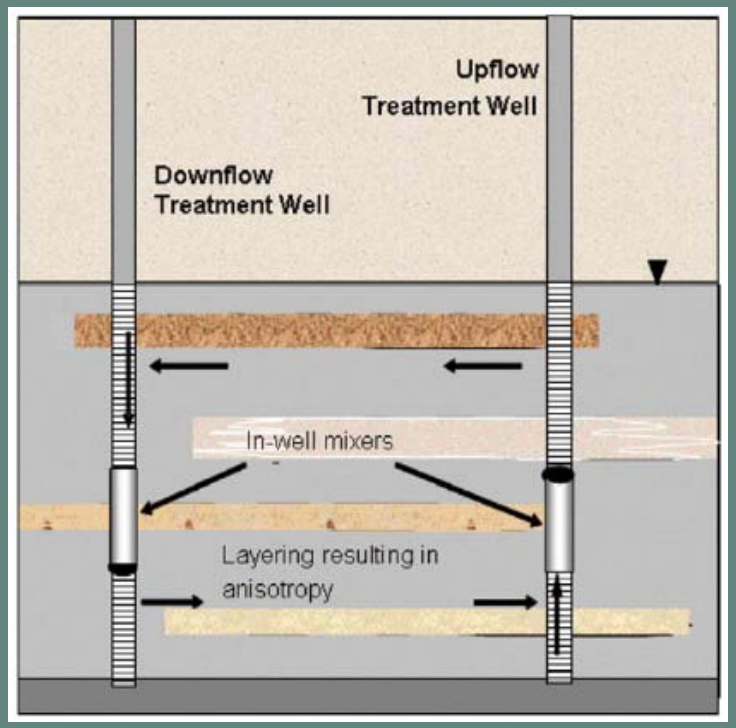


Bae et al., 1995



McCarty et al., 1998; Goltz et al., 2009

CURRENT EFFORT

Puerto Rico TestSite for Exploring Contamination Threats (PRoTECT)

Superfund Research Program

PI/Co-Director: Akram N. Alshawabkeh,
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Northeastern University

University of Puerto Rico – Medical Sciences Campus

University of Puerto Rico – Mayagüez

University of Michigan

Northeastern

http://www.northeastern.edu/protect

NIEHS
National Institute of Environmental Health Sciences – National Institutes of Health

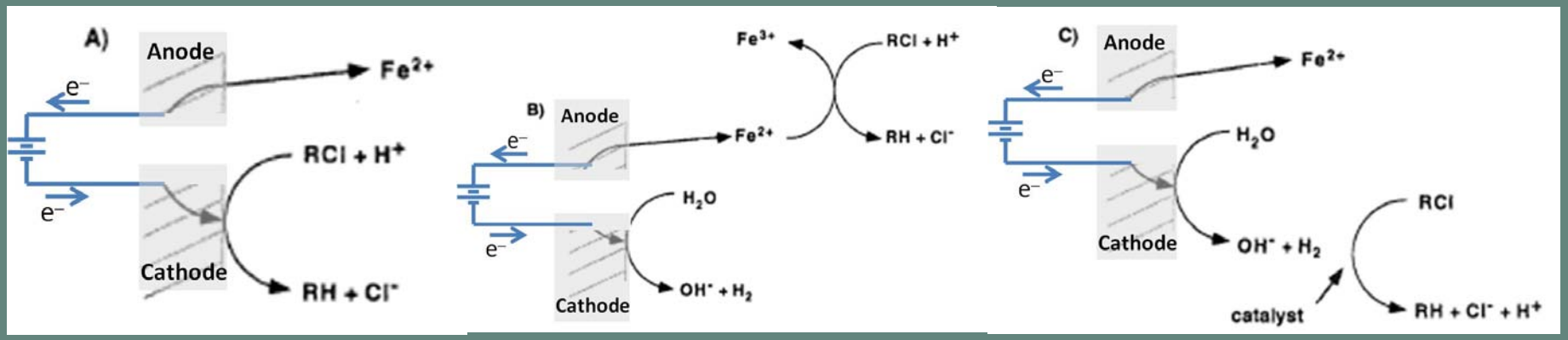
PROTECT Focus

- Role of exposure to contamination on preterm birth
- Contamination in Puerto Rico (14 Superfund site + 2 Proposed)
- karst aquifers
- Target Contaminants: Chlorinated Solvents and Phthalates

PROTECT Project 5

Alshawabkeh, Padilla, Podlaha, Vesper

- Goal: Developing green remediation technologies based on conversion of solar energy into electrochemical redox in groundwater
- Focus on chlorinated solvents in karst aquifers
- Proposed transformation pathways:



SUMMARY AND ACKNOWLEDGMENT

Summary

- Solar energy conversion into electrochemical redox in groundwater can be a green and sustainable remediation technology
- Oxidizing or reducing groundwater conditions can be engineered
- Conditions can be developed for chemical, biological and/or electrochemical transformation
- Fe anodes would lead to reducing conditions causing reduction and immobilization of chromium
- Transformation of chlorinated solvents by iron electrodes is being evaluated in karst aquifers

Acknowledgment

- PRoTECT Team and Advisory Committees
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NIEHS National Institute of Environmental Health Sciences

Srp Superfund Research Program

Looking Into Hidden Worlds CenSSIS

PROTECT Team