ARCADIS
Infrastructure, environment, facilities

Phase II Kickoff Meeting Presentation

Cost Effective In-situ Groundwater Remediation of DOE High Level Sites with Enhanced Anaerobic Reductive Precipitation/Enhanced Reductive Dechlorination: Hanford 200-UP-1

October 2007

Agenda

Project Overview Briefing

- Introduction, Project Scope and Tasks
- Background: Overview of Technology
  - Applications to Technetium and Nitrate
- Hanford 200-UP-1: Specific Activities
  - Technical Objectives
  - Conceptual Site Model
  - Pilot System Design
  - Bench-Scale and Tracer Tests

Introduction
Project Scope and Tasks

ARCADIS' ART Phase II Project

- In ART Phase II, DOE has ordered a demonstration at Hanford Site 200-UP-1 budget $3.65M over 5 years
- DOE is considering an option for Savannah River Site Area F that budget would be $1.61M over 5 years
- Hanford 200-UP-1-S-SX
- Located on the Plateau in the 200-West area
- Key constituents of concern are technetium-99, nitrate, chromium
- Three injection wells and four new monitoring wells planned
- Planned reagents molasses and ferrous sulfate

General Program Objectives

- **Overall objective**: to demonstrate that a widely used, commercially available, in-situ remediation technology, Enhanced Anaerobic Reductive Precipitation (EARP)/Enhanced Reductive Dechlorination (ERD) can provide cost-effective groundwater remediation for DOE High Level Waste Sites
  - EARP/ERD has already been used at 190 sites, including 21 Federal sites, for a wide variety of metals, energetics, chlorinated organic compounds, nitrate and uranium.
  - Geochemical laboratory measurements and limited field tests (many sponsored by DOE under the NABIR program) have shown that this technology can be applied to other key radionuclides. However, this technology has yet to be applied at field scale for radionuclides at a DOE facility.
- **Specific application objective**: to demonstrate field-scale applications to key radionuclides present in high level waste impacted groundwater, such as technetium-99, neptunium, strontium-90, iodine-129, and uranium. Metals (e.g., mercury, chromium) and CAHs are also of interest.

Fit to DOE Needs

This technology meets a number of high priority needs discussed in the Office of Environmental Management's "Technology Development and Deployment Plan" of August 2004:

- "Groundwater and soils contamination, which reflects the significance of this issue at every cleanup site….Inherent to this problem are the long-lifetime contaminants of concern --- radionuclides (Tc, Np, Pu), mercury and other toxic metals and organics."
- "In-situ methods of treatment may be the only way to address remediation of persistent and toxic metals, principally mercury and longer-lived radionuclides"
- Numerous sites at Hanford and Savannah River to which this technology is applicable have been identified in our proposal

Basic Activities for Any Phase II Site

- Work plan, QAPP, HASP, etc.
- Permitting in coordination with host facility/contractor
- Tracer testing for reagent delivery (qualitative and quantitative tracers)
- Staggered well installation, injection system installation
- Treatment for up to 2 years as necessary
- Process and biogeochemical monitoring
- 18 months post-treatment of rebound observation
- Data analysis, interim reporting and final reporting

Deliverables

- UIC Class V Permit may be required
- Excavation Permit
  - including an assessment of cultural and biological resources
- Drilling Permit
- Health and Safety Plan
- Project plan/QAPP
- Monthly Reports
- Final Project Report

Projected Schedule

- Permitting and Work Plans
  - Draft plans/permit applications completed 12/07, final plans 1/08
  - Clearance needed to proceed with tracer test 2/08
- Well Installation and Initial Tests
  - Initial well installation 3/08
  - Bench-scale and tracer tests 4/08 to 10/08
  - Additional wells and injection system installation 10/08 to 1/09
- Pilot Test
  - Reagent injections 2/09 to 12/10
  - Six process monitoring events 5/09 to 10/10
  - Four biogeochemical monitoring events 3/10 to 8/12
    - Includes 2 post-treatment “rebound” events
- Final Report
  - Draft report 7/12, final report 9/12

Safety Project Training Requirements

- Current OSHA 40-hr Hazardous Waste Operator Training (HAZWOPER) and at least one of the field personnel will have current Hazardous Waste Site Supervisor and First Aid/CPR training.
- All field personnel will participate in a medical monitoring
- ARCADIS has established radiological control (RADCON) and “As Low As Reasonably Achievable” (ALARA) programs to minimize exposures to radiation and radioactive material.
- Prior to entry each ARCADIS and subcontract employee shall attend Hanford General Employee Training.
- All field personnel involved with drilling and sampling of environmental media will attend and successfully pass Hanford’s Radiological Worker training.

IDW Disposal

- 200-UP-1 has several years of characterization data that can be utilized for waste designation
- Contaminated solid waste, soils and slurries that meet the Hanford Environmental Restoration Disposal Facility (ERDF) waste acceptance criteria will be disposed at the ERDF
- Contaminated liquids may be sent to the Purgewater Storage and Treatment Facility (PSTF) or Effluent Treatment Facility (ETF).
- Small volumes of stabilized liquids may be disposed at the ERDF provided the waste acceptance criteria can be met
- Waste that does not meet the acceptance criteria may be stored at the Central Waste Complex (mixed waste) or sent offsite for disposal (nonradiological waste), provided EPA has made an offsite determination per 40 CFR 300.440
- Wastes may be treated in the operable unit or at the ERDF to meet disposal facility waste acceptance criteria
- Liquids below purgewater collection criteria as identified in the *Strategy for Handling and Disposing of Purgewater at the Hanford Site, Washington* (July 1990) may be discharged to the ground
- Miscellaneous solid waste and demolition debris that is non-hazardous and has been radiologically released may be disposed to an offsite solid waste landfill or onsite demolition landfill

Background
Overview of Technology

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Introduction to this Technology

- In situ addition of carbohydrate substrate to create reactive zones is a commercially developed, patented technology (U.S. Patent Nos. 5,554,290; 6,143,177; 6,322,700 and 6,632,364 and others)
- Known for metals and radionuclides as Enhanced Anaerobic Reductive Precipitation (EARP)
- Known for CAHs as Enhanced Reductive Dechlorination (ERD)
- EARP and ERD are described generally as In situ Reactive Zones (IRZs)
- Introduction of an innocuous, food-grade carbon substrate (typically molasses or whey) to groundwater
- Produces anaerobic conditions through microbial action

Chemical Reduction & Formation of Insoluble Precipitates

- Oxidized metals such as Cr (VI) are reduced
- Precipitates can be formed in-situ either as hydroxides, carbonates or sulfides. Sulfide will be present in the groundwater as a result of the microbial reduction of sulfate occurring naturally in the groundwater at contaminated sites or as a component of the injected molasses solution. Co-precipitates can also be formed.

Mechanism for the Reduction & Formation of Insoluble Precipitates

For example, Cadmium

$$Cd^{2+} + S^{2-} \square CdS\ (s)$$

or

$$Cd^{2+} + CO_3^{2-} \square CdCO_3\ (s)$$

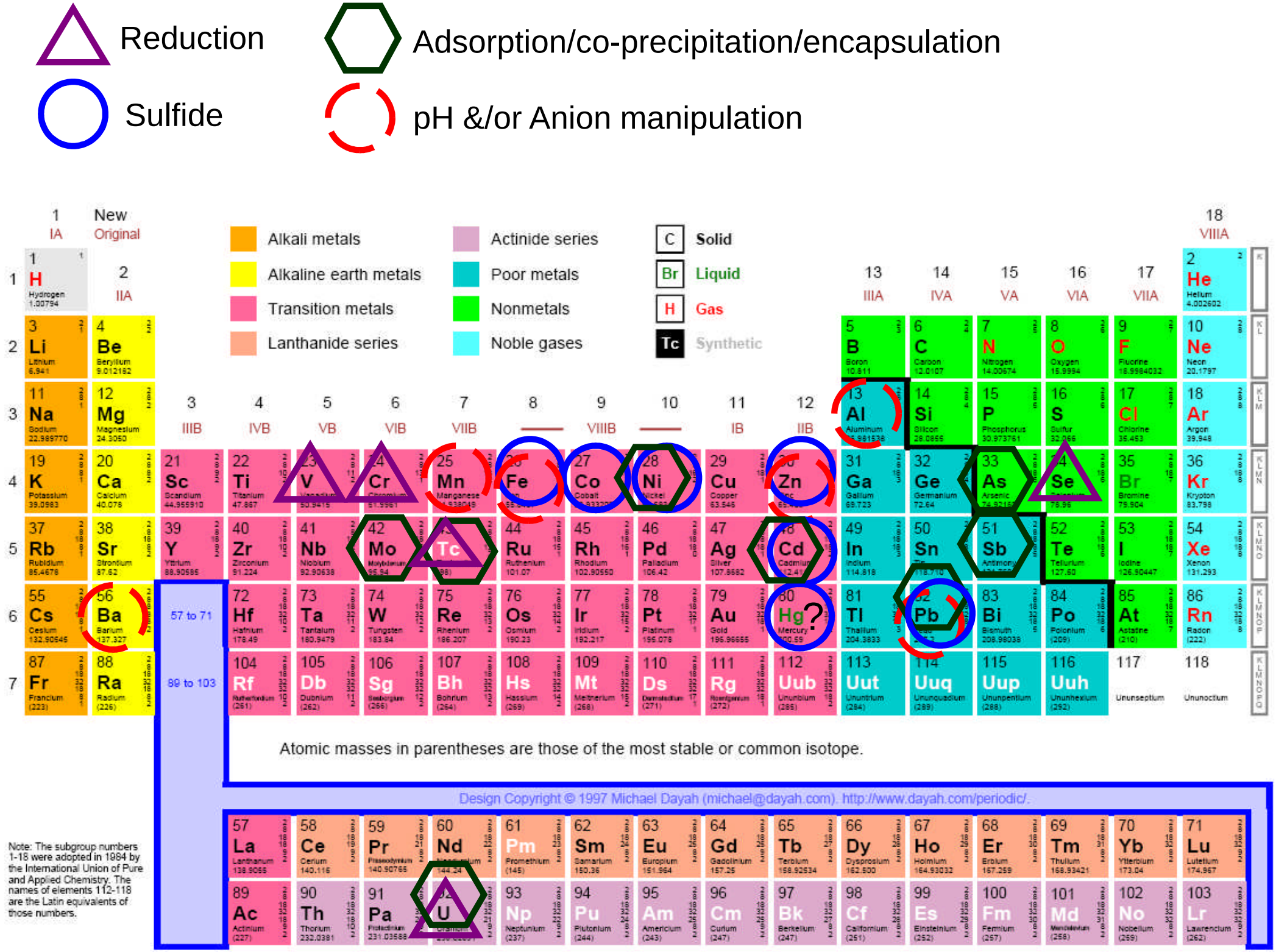
For example, Chromium

$$HCrO_4^{-} + 3Fe^{+2} + 7H^{+} \rightarrow Cr^{+3} + 3Fe^{+3} + 4H_2O$$

$$2Cr_2O_7^{-2} + 3C^0 + 16H^{+} \rightarrow 4Cr^{+3} + 3CO_2 + 8H_2O$$

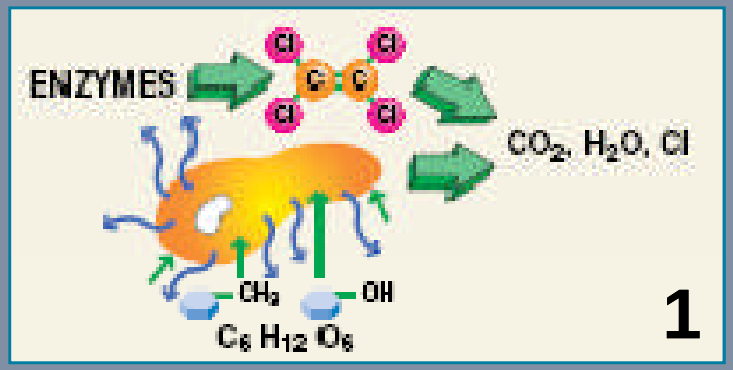
$$Cr^{3+} + 3\ H_2O \rightarrow Cr(OH)_3\downarrow + 3\ H^{+}$$

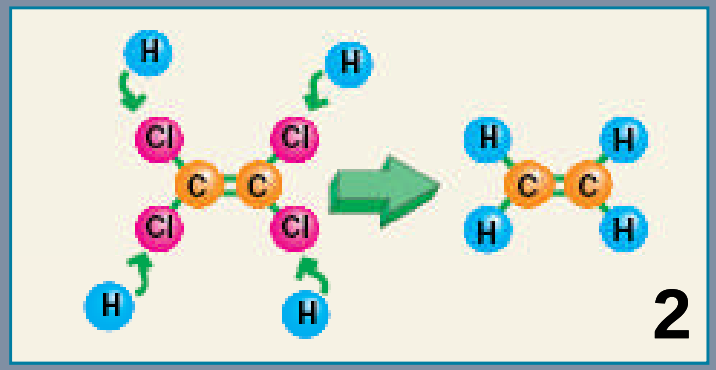
Hydroxide $K_{sp} = 6.7 \times 10^{-31}$

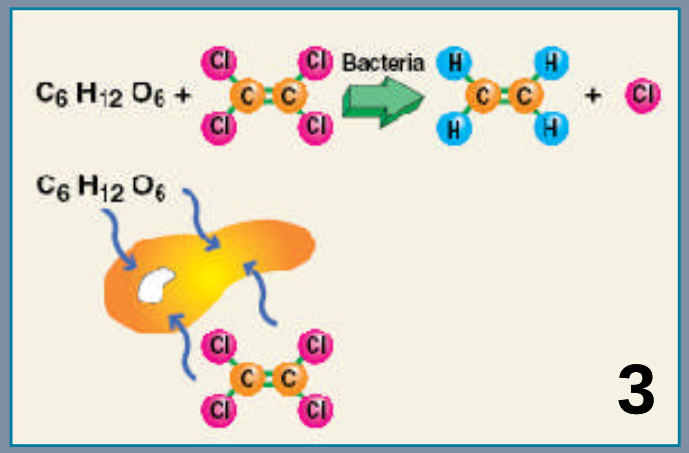

Reduction
Adsorption/co-precipitation/encapsulation
Sulfide
pH &/or Anion manipulation
1 New
IA Original
18
VIIIA
Alkali metals
Alkaline earth metals
Transition metals
Lanthanide series
Actinide series
Poor metals
Nonmetals
Noble gases
C Solid
Br Liquid
H Gas
Tc Synthetic
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIIIB
10
11 IB
12 IIB
57 to 71
89 to 103
Hg?
Atomic masses in parentheses are those of the most stable or common isotope.
Design Copyright © 1997 Michael Dayah (michael@dayah.com). http://www.dayah.com/periodic/.
Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

Mechanisms of degradation of chlorinated aliphatic hydrocarbons

(1) Cometabolism, (2) Hydrogenolysis, (3) Dehalorespiration







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Mobile Batch Injection Trailer

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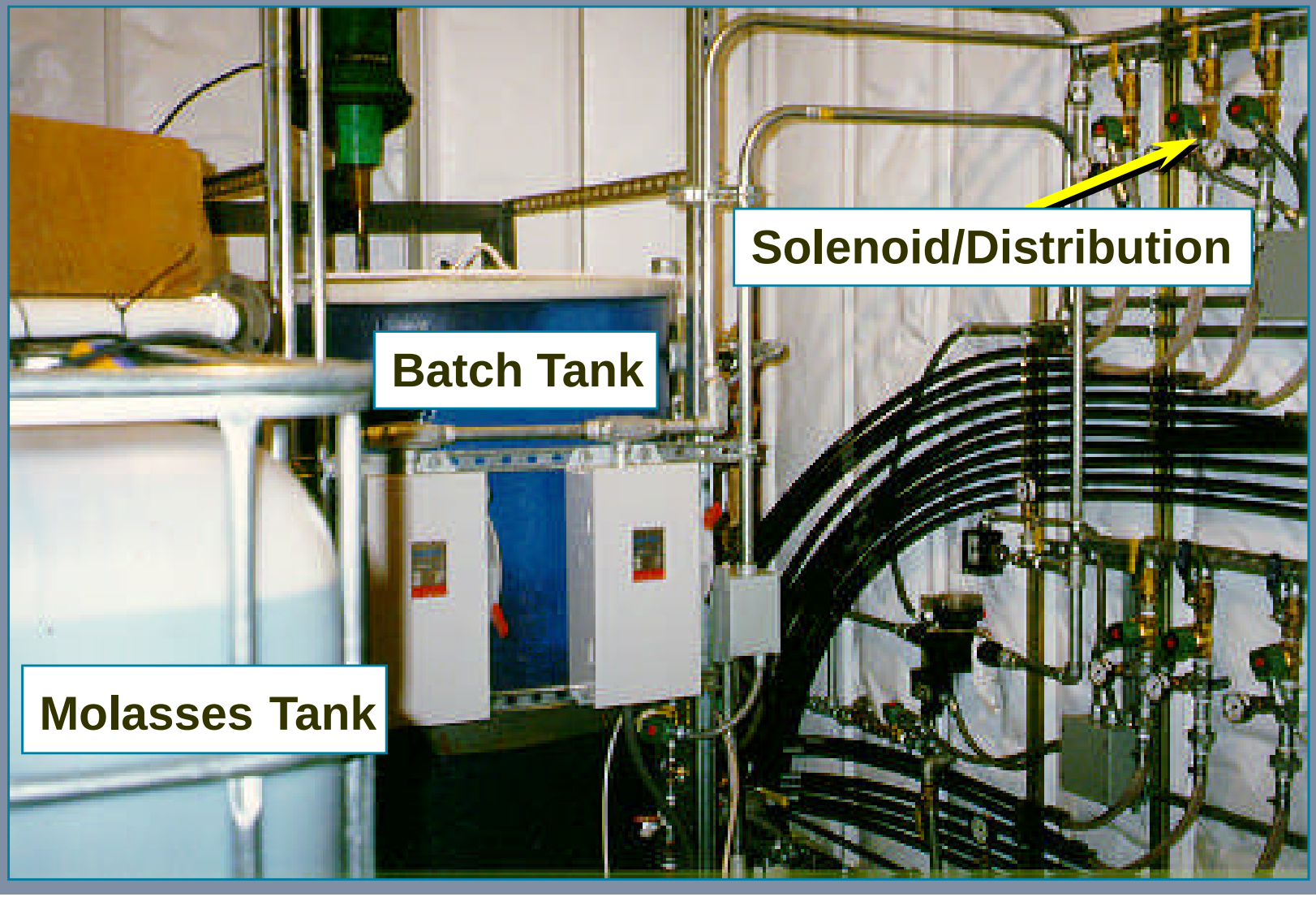
Fixed, Automated Injection System



Contaminants Treated to Date

- PCE, TCE, DCE, VC, TCA, CT, CF, trichlorofluoromethane
- U, Cr^{+6}, Ni, Cd, Pb, Hg, Zn
- PCP, pesticides, chlorinated propanes
- RDX, TNT, perchlorate

<u>Concentrations</u>

- Total CAHs 0.1 to 296 mg/L (majority PCE or TCE sites)
- Cr^{+6} up to 140 mg/L

Contaminants Treated

Category	Number of Sites
CAHs	146
PCE/TCE/DCE/VC	132
TCA/DCA	21
CT/CF/MC	7
Other Contaminants	
Perchlorate	9
Explosives	2
Uranium	2
Chromium	20
Other metals (Zn, Cd, Pb, Ni, Hg)	8

Variety of Applications

Ownership

- >170 commercial/industrial sites
- 21 sites underway at 16 Federal facilities
  - DoD and others
- 27 sites under contract at 20 Federal facilities
  - The majority of these are performance-based contracts at DoD facilities

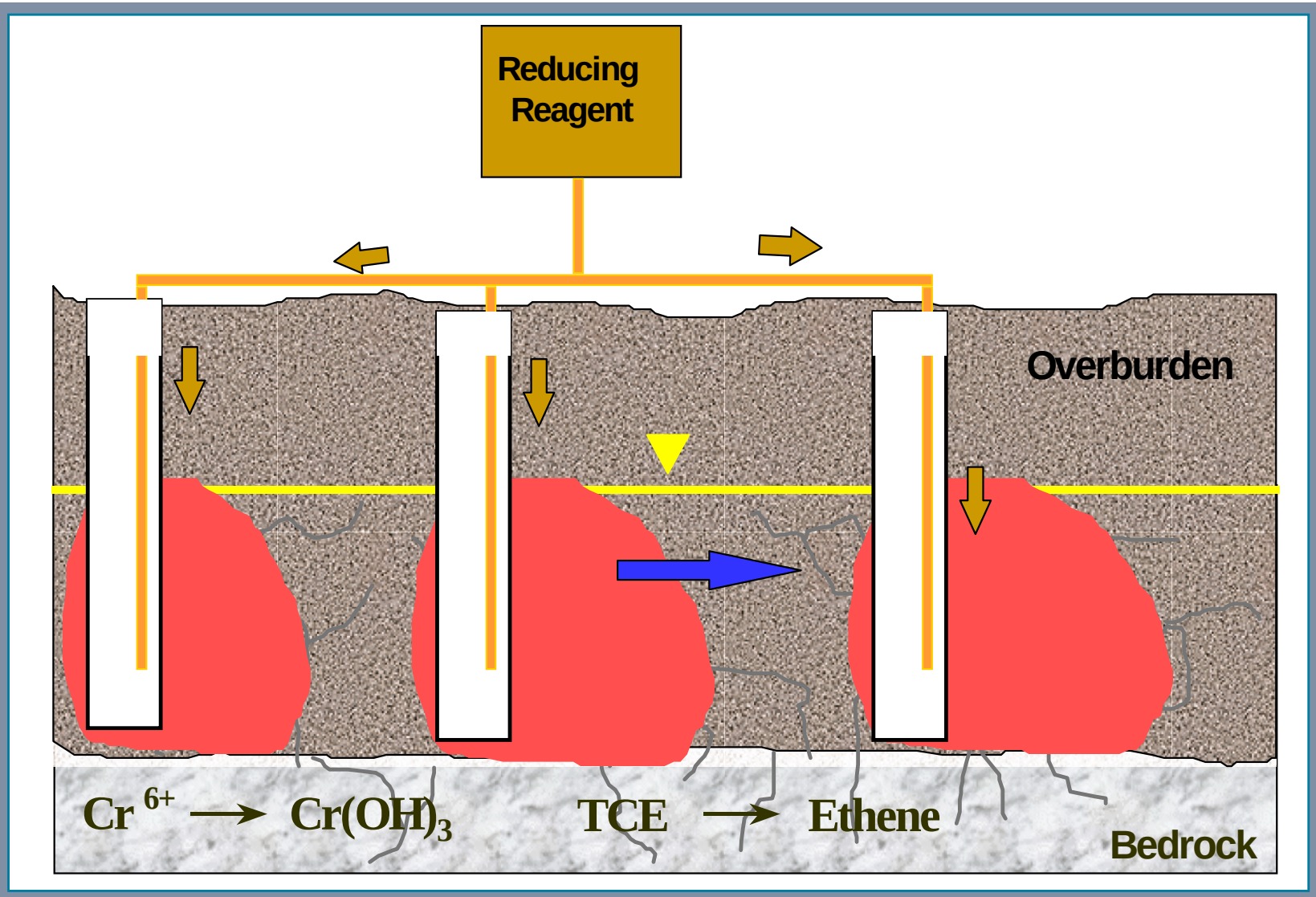
Variety of Applications

- Geometries
  - Source zones, barriers, or plume-wide
- Sizes
  - small pilots to 50 acres
- Geologic & hydrogeologic settings
  - Unconsolidated sediments
    - Highly permeable sands & gravels to low-permeability clays
  - Partially weathered rock
  - Fractured bedrock
  - K range 10^{-6} to 10^{0} cm/s (10^{-3} to 10^{3} ft/d)

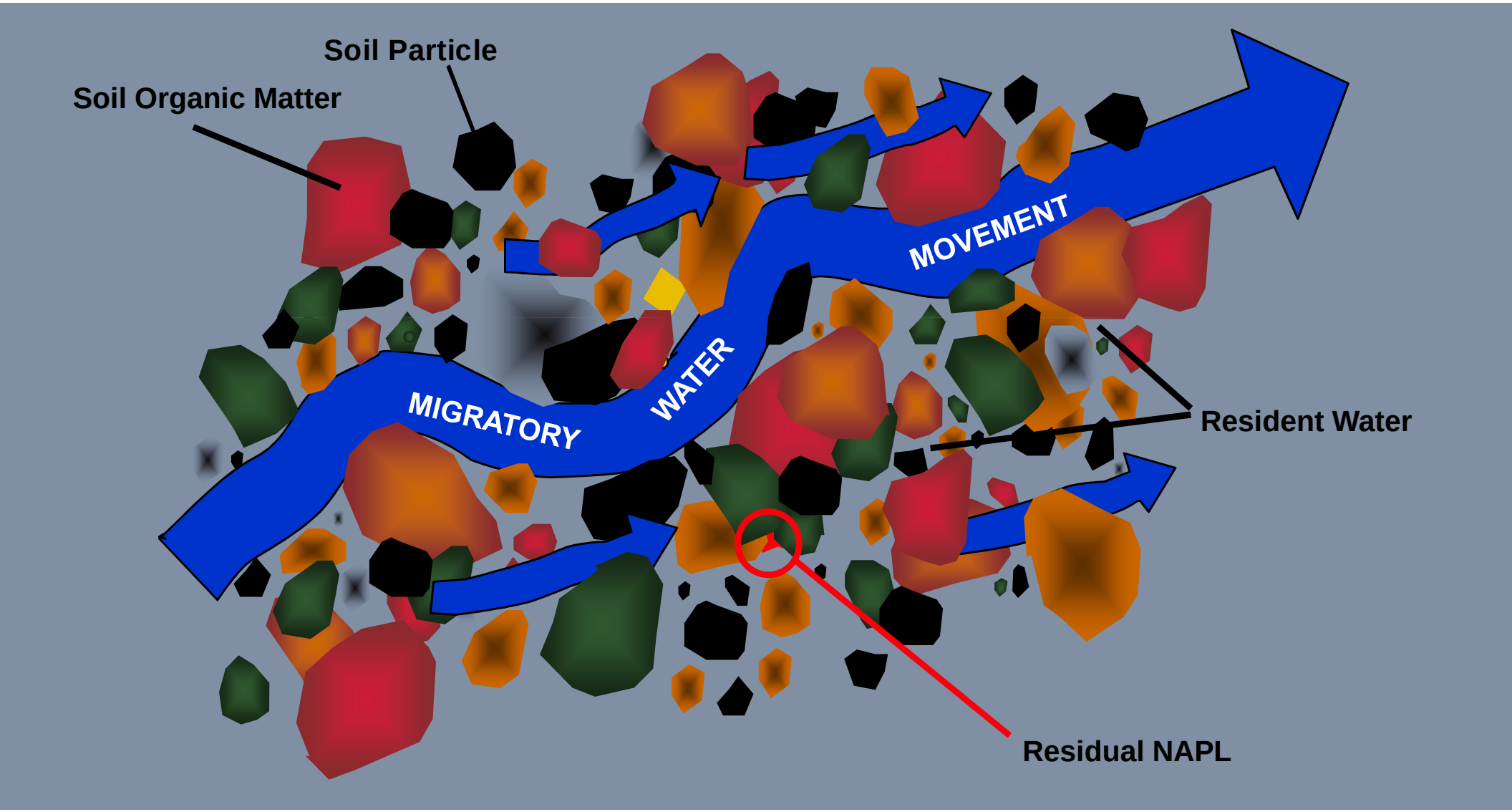
Strategies Vary for Different Constituents

- Strongly reducing conditions are preferred for CAHs
- Mildly reducing conditions may be preferred for some other constituents such as nitrate, perchlorate, and perhaps RDX
- Some metals can be precipitated with carbohydrate only, but others such as arsenic and uranium require iron coprecipitation to prevent resolubilization
- Introduction of ferrous iron in such systems is known as the Saunders process (Vadose Zone Journal 2:177-185 (2003), Bioremediation Journal Volume 9, #1, p33-48, (2005); US Patent 5,833,855)

Schematic Diagram – Cutaway View Reducing Reactive Zones



The Multi-Porosity Aquifer Matrix – Mobile and Immobile (or less mobile) fractions



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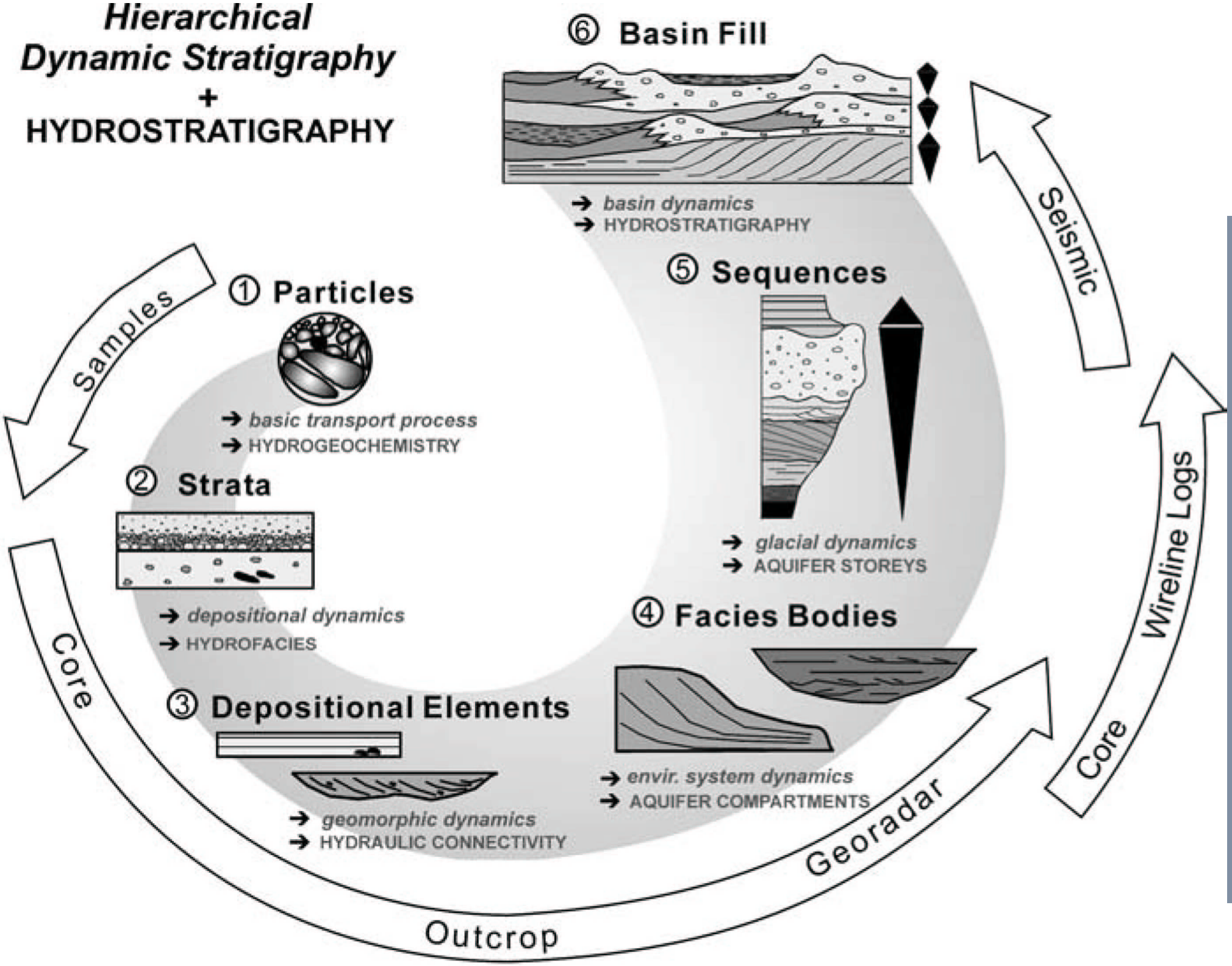
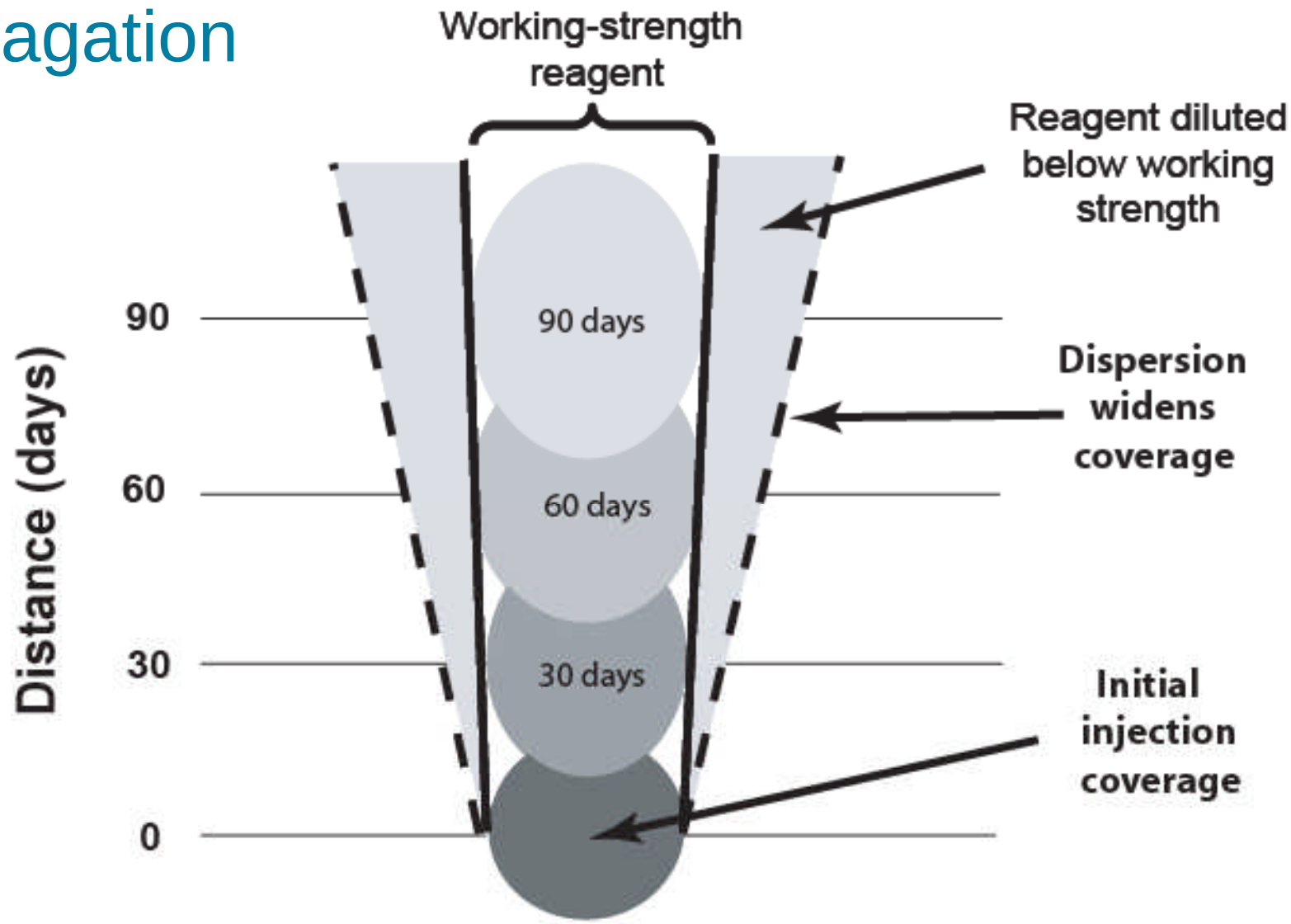

Hierarchical
Dynamic Stratigraphy
+
HYDROSTRATIGRAPHY
⑥ Basin Fill
→ basin dynamics
→ HYDROSTRATIGRAPHY
⑤ Sequences
→ glacial dynamics
→ AQUIFER STOREYS
④ Facies Bodies
→ envir. system dynamics
→ AQUIFER COMPARTMENTS
③ Depositional Elements
→ geomorphic dynamics
→ HYDRAULIC CONNECTIVITY
② Strata
→ depositional dynamics
→ HYDROFACIES
① Particles
→ basic transport process
→ HYDROGEOCHEMISTRY
Samples
Core
Outcrop
Georadar
Core
Wireline Logs
Seismic

Reactive zone propagation



Publications

- The successful application of IRZ technology has been reported and summarized in more than seventy papers and book chapters
- At least 35 IRZ sites have been published in the open literature
- An ERD protocol document, co-funded by ESTCP and AFCEE, is available on the ESTCP website
- Suthersan and Payne *In-situ Remediation Engineering*, CRC Press, 2005 has extensive technical discussions

Technetium and Nitrate Mechanism of IRZ Treatment

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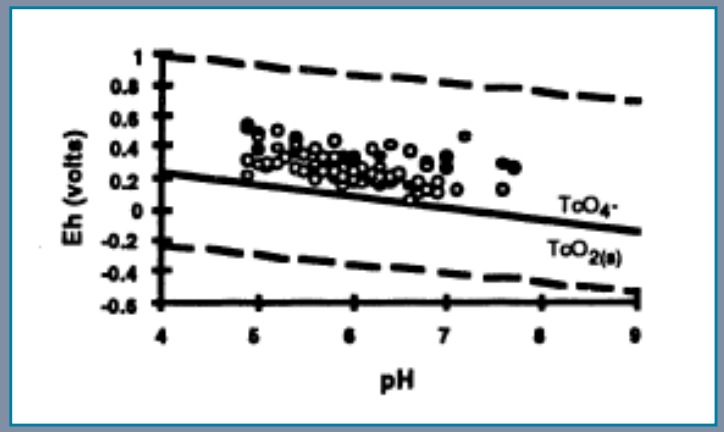
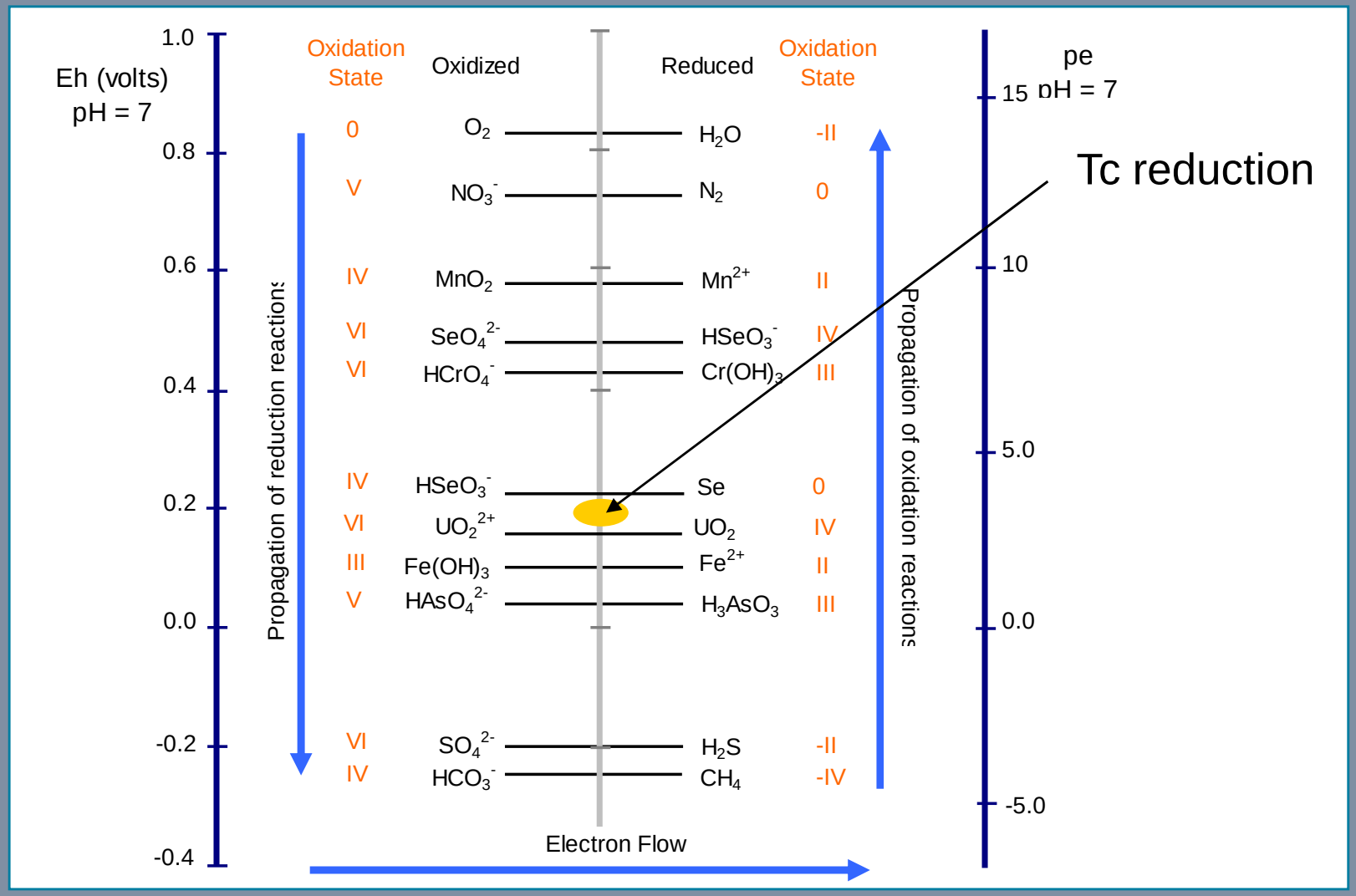
Technetium Geochemistry

- Two ionic states: Tc(VII) and Tc(IV)
  - Tc(VII) [e.g., TcO_4^-] more soluble and mobile
  - Tc(IV) [e.g., hydrous TcO_2] insoluble and immobile:
    - $TcO_2 \cdot 1.6H_2O \leftrightarrow TcO(OH)_{2(aq)} + 0.6\ H_2O$; logK = -8.4
- Tc(VII) can be transformed to Tc(IV) by
  - Abiotic reduction
  - Microbial reduction
    - $TcO_4^- + 4H^+ + 3e^- \leftrightarrow TcO(OH)_{2(aq)} + H_2O$
- Complexes with ligands:
  - Carbonate = $Tc(IV)CO_3(OH)_{2(aq)}$
  - TBP, organic ligands, natural organic matter



Sequence of Electron Donor Utilization



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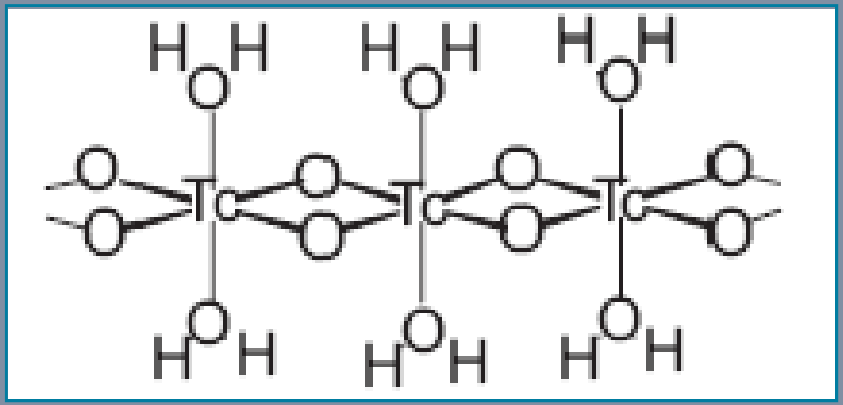
Reduction of Tc(VII)

- Requires strong (e.g., Fe) reducing condition
- Reduction occurs concurrently with Fe(III) reduction
- Direct enzymatic action or indirect (FeS)
- Requires nitrate reduction to be complete
- Studies suggest Mn reduction must be complete as well (Zachara, GCA2004)

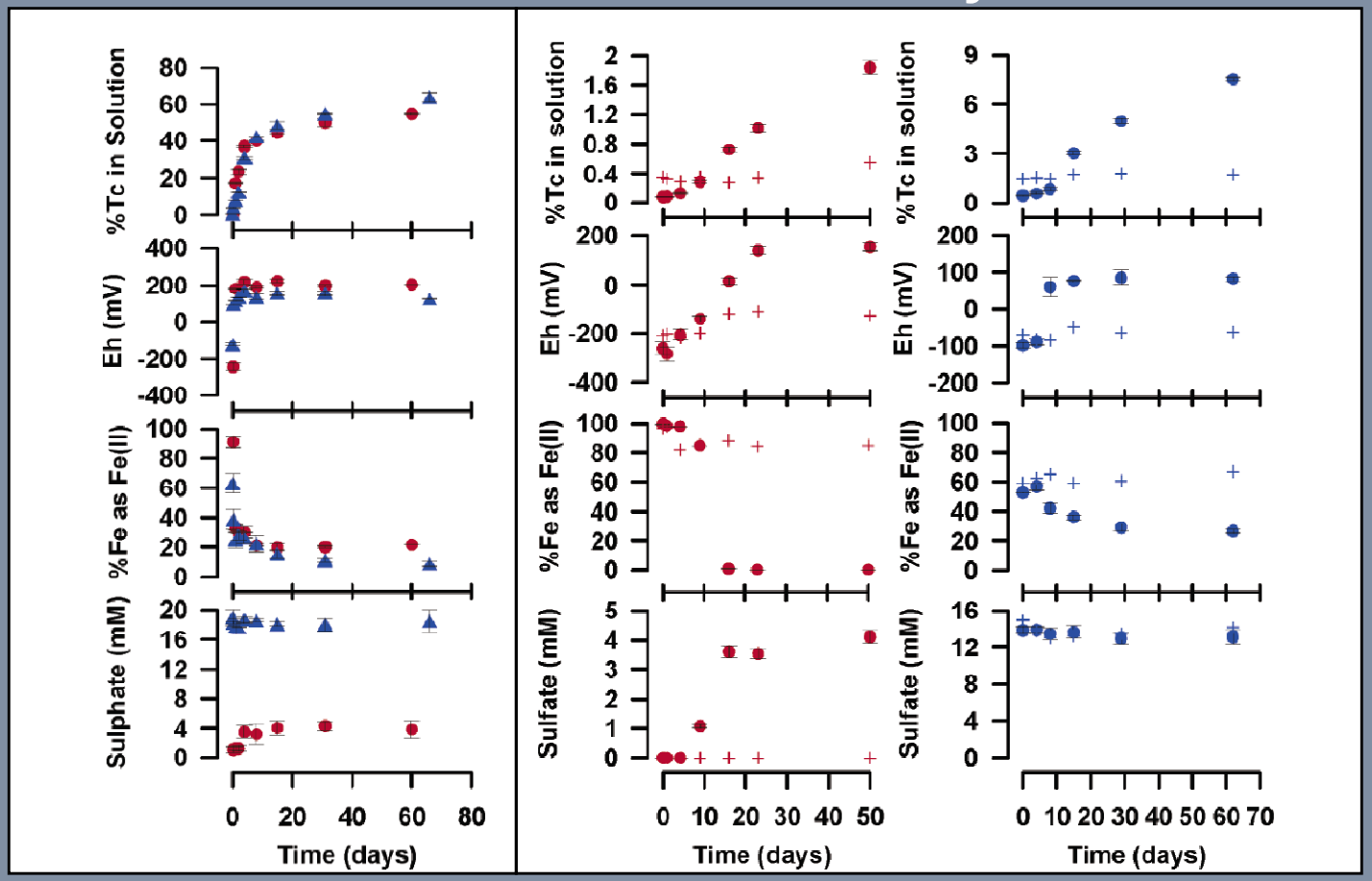


Reoxidation of Tc(IV)

- Reoxidation by nitrate (or other oxidants)
  - About 50% reoxidation can occur
  - Both Tc(VII) and Tc(IV) remain immobilized
- Reoxidation by air
  - Most favorable under aerobic condition
  - Significant remobilization of Tc(VII) occurs

In-Situ Remediation Challenge: Preventing Tc Remobilization

Constant Aeration **Oxidation by Nitrate**



Blue *= reduction proceeded to iron reducing conditions*
Red *= reduction proceeded to sulfate reducing conditions*

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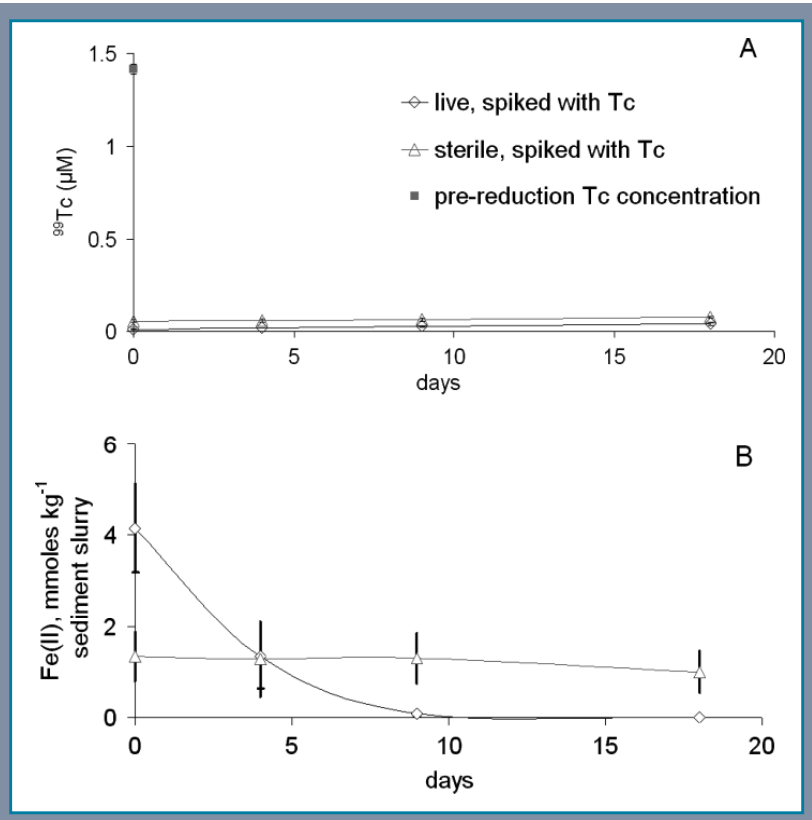
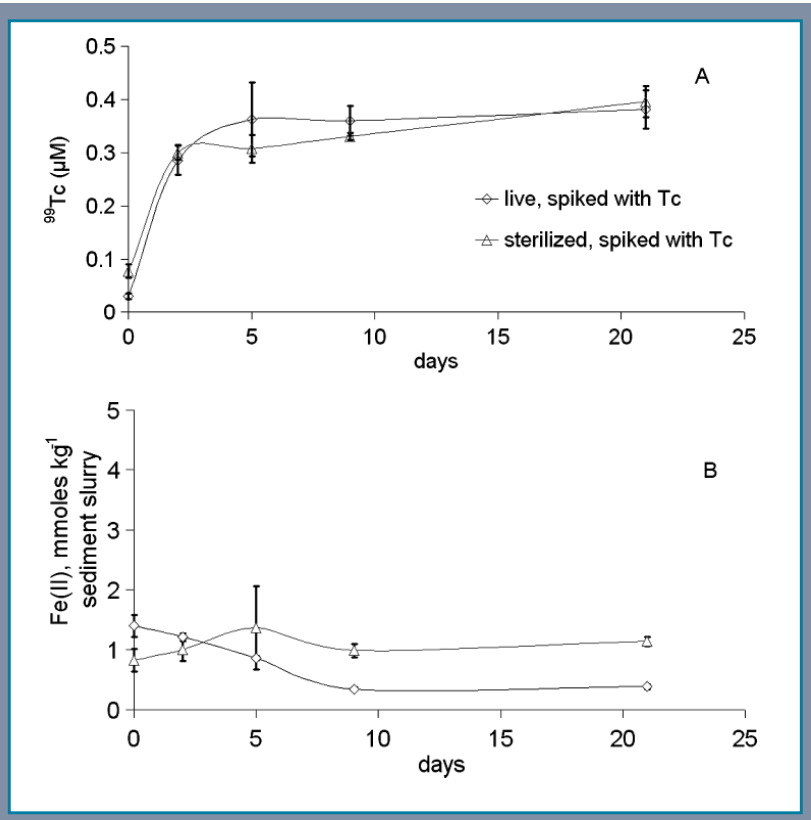
Estuarine sediments, Burke, et al., ES&T 2006

Remobilization of Tc



Reoxidation of pre-reduced Fe(II)/Tc(IV)-bearing FRC sediments with 100 mM nitrate. A: concentration of soluble 99Tc (*µ*M), B: concentration of acid (0.5 N HCl) extractable Fe(II) (mmoles kg−1 sediment slurry).



Reoxidation of pre-reduced Fe(II)/Tc(IV)-bearing FRC sediments with air. A: concentration of soluble 99Tc (*µ*M). B, concentration of acid (0.5 N HCl) extractable Fe(II) (mmoles kg−1 sediment slurry).

Biogeochemical cycling of Tc is strongly correlated with exposure to oxygen, and under anaerobic oxidation condition, TC(IV) does not remobilize even in the presence of high concentration of oxidants (e.g., nitrate)

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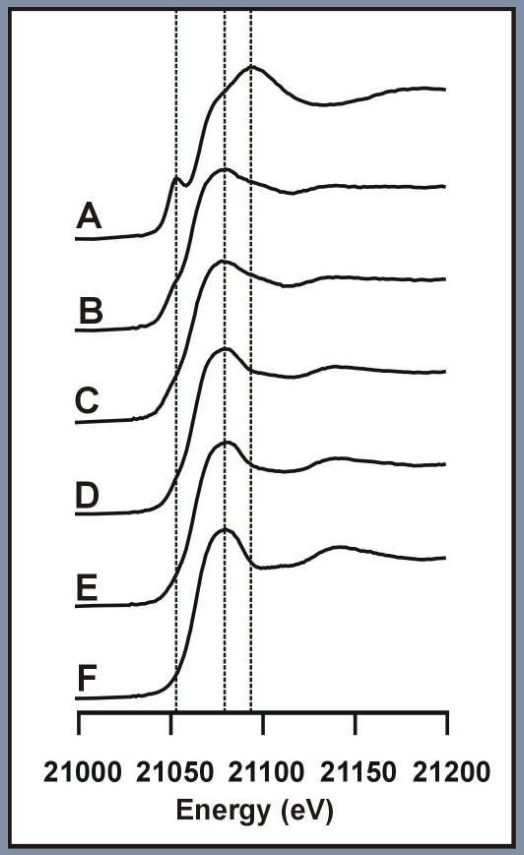
McBeth, J. M. and Lear, G, “Technetium Reduction and Reoxidation in Aquifer Sediments”, *Geomicrobiology Journal*, July 2007.

Characterization of Tc

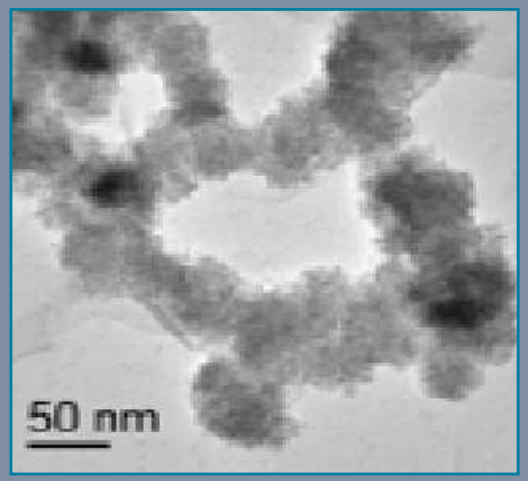
- Radioanalytical = beta LSC
- Chemical
  - Selective extraction
  - Solid-state analysis (XRF, XAS)
- Tc K-edge (21,044 eV)
  - A=Tc(VII)
  - B-F
    (Tc(IV) formed by bioreduction)

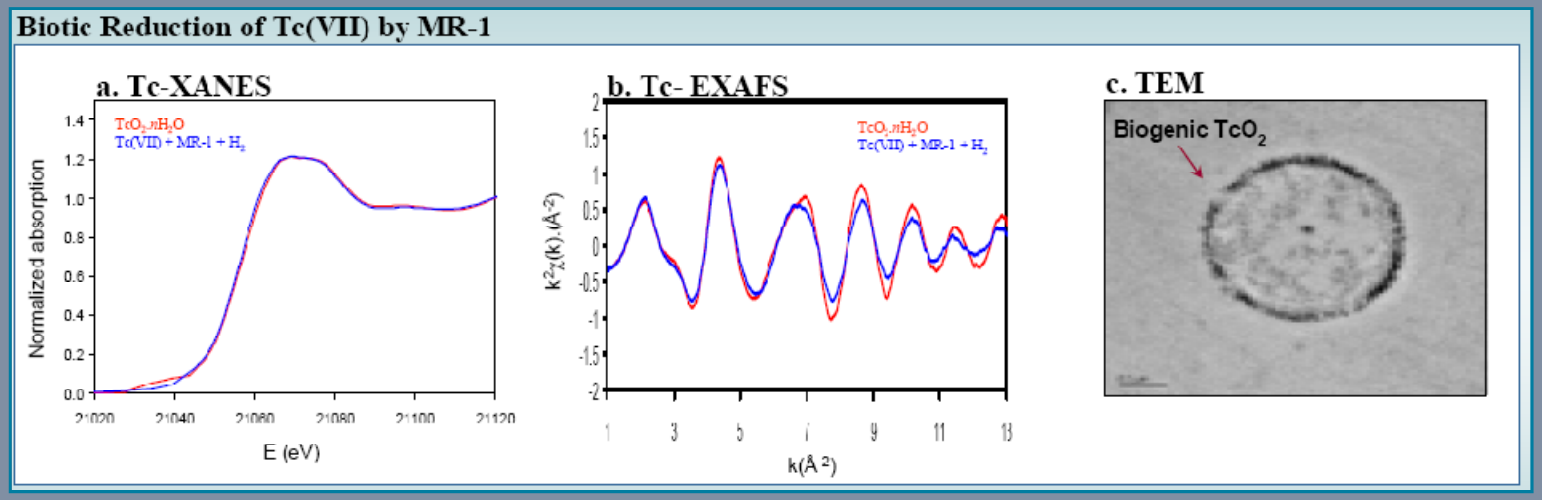


Role of Iron

- Recent work by Zachara (PNNL) shows:
  - Fe(II) can reduce Tc(VII)

    $Tc(VII)O_4^- + 3Fe^{2+} + (n+7)\ H_2O = Tc(IV)O_2 \bullet nH_2O + 3\ Fe(OH)_3(s) + 5H^+$
  - Tc reduced by Fe(II) forms an Fe(III)/Tc(IV) precipitate





Denitrification under anaerobic conditions

- Nitrate is reduced through intermediates such as nitrite or nitrous oxide and subsequently to nitrogen gas
- Nitrate is the most favored electron donor after dissolved oxygen and thus is readily utilized in the presence of an electron donor such as a carbohydrate
- Can be accomplished in-situ by numerous organisms such as *Micrococcus, Pseudomonas, Denitrobacillus, Spirillum, Bacillus, Acromobacter, Acinetobacter*, etc.
- Process is widely used in ex-situ wastewater treatment, and is a necessary intermediate step in most anaerobic IRZs
- In this case nitrate is also a constituent of concern

Hanford 200-UP-1
Specific Activities

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Site-Specific Objectives 200-UP-1

- Demonstrate effective distribution of reagents to the Ringold formation gravels
- Demonstrate that reducing biogeochemical conditions can be induced and sustained for a treatment period (i.e., 18 months to 2 years)
- Demonstrate that the concentration of key COCs in the groundwater can achieve treatment goals in 2 years or less in the reactive zone:
  - technetium-99 drinking water standard (900 pCi/L) – this is below the interim remedial goal of 9,000 pCi/L
  - nitrate drinking water standard (45 mg/L)
  - chromium remediation goal (22 µg/L)
  - carbon tetrachloride MCL (5 µg/L)
- Demonstrate that the precipitated technetium and chromium remain in insoluble forms. Note: we expect a continued flux of these radionuclides from upgradient.
- Show that secondary water quality impacts of the EARP technology are limited spatially downgradient of the reactive zone

Conceptual Site Model

- SX Tank Farms (underground 1M-gal tanks)
  - In service 1954-1980 (~26 years); many leaked
  - Received REDOX Plant waste, first-cycle condensate and REDOX high-level boiling waste
  - All have been “interim isolated” but still there is a vadose zone source within the fence
- Key contaminants
  - Technetium-99 (18,000 pCi/L)
  - Chromium (250 ug/L)
  - Nitrate (110 mg/L)
  - Carbon tetrachloride (50 ug/L)
    - originates from 200-ZP-1

Conceptual Site Model
(continued)

- Target zone is the uppermost portion of the unconfined aquifer within the Ringold Unit E “gravels”
  - Fluvial, gravel-dominated sediments with a fine-sand matrix (PNNL-13514)
  - Sandy gravel, variable cementation reported at 299-W22-47 (PNNL-15775)

Conceptual Site Model
(continued)

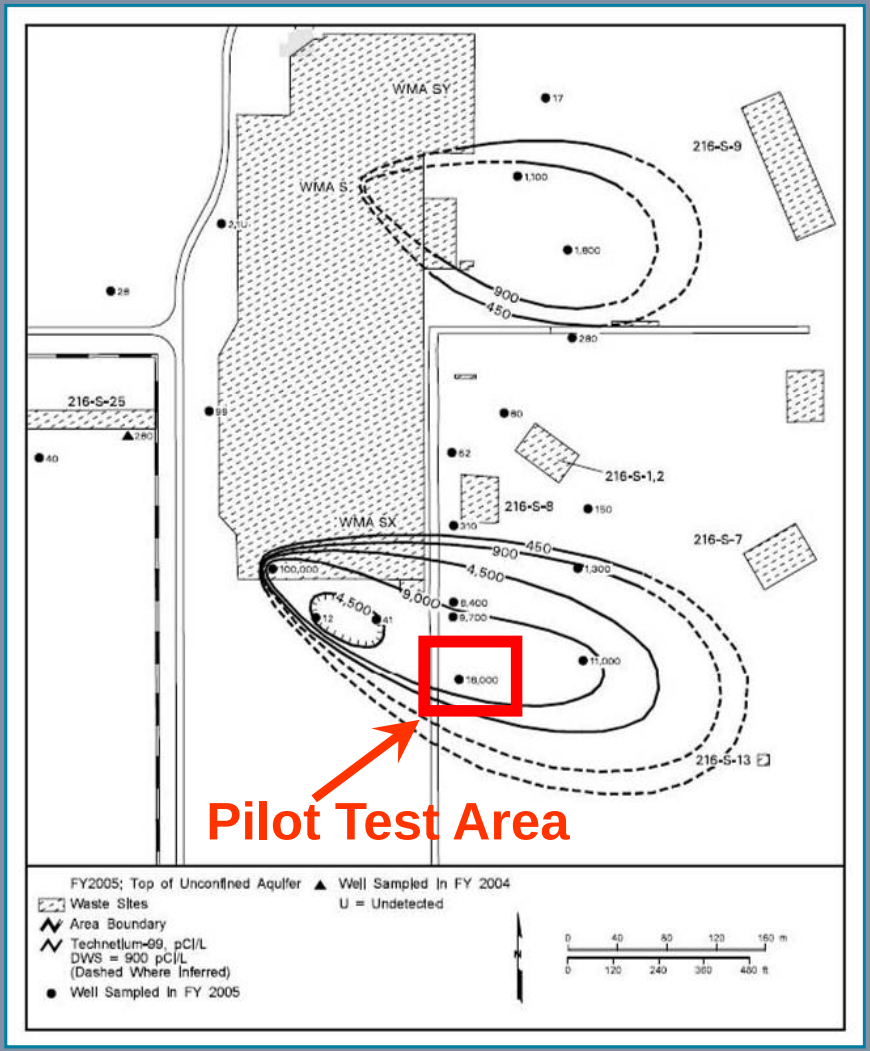
- Hydrogeologic characteristics of target aquifer
  - Flow direction: to the east-southeast
  - Depth to water 69 m (228 ft)
  - Saturated thickness ~ 40 m (130 ft)
  - K ~ 0.78 to 5.7 m/d (2.5 to 19 ft/d)
  - Velocity ~ 0.07 to 0.14 m/d (0.23 to 0.46 ft/d)
    - Based on tritium travel times during P&T operations at adjacent site, but consistent with other calculated values
  - Contaminant levels highest in the upper part of the aquifer

Conceptual Site Model
(continued)

- Groundwater Chemistry
  - Average pH is slightly basic, ~7.9
    - Based on an average alkalinity of 90 mg/L
  - DO 9.9 mg/L
  - Nitrate 110 mg/L
  - Sulfate 16.8 mg/L
  - Dissolved iron and manganese are low

Average Technetium-99 Concentrations at Waste Management Area S-SX

Top of Unconfined Aquifer (PNNL-15670)



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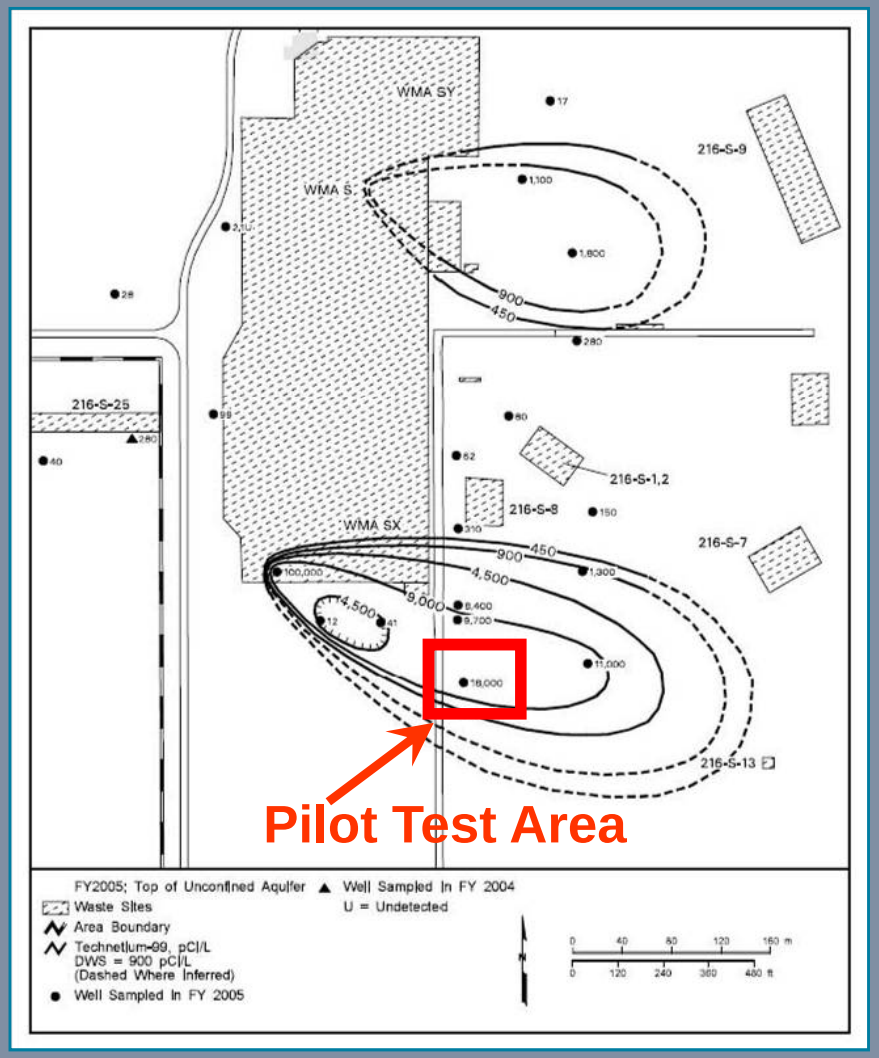
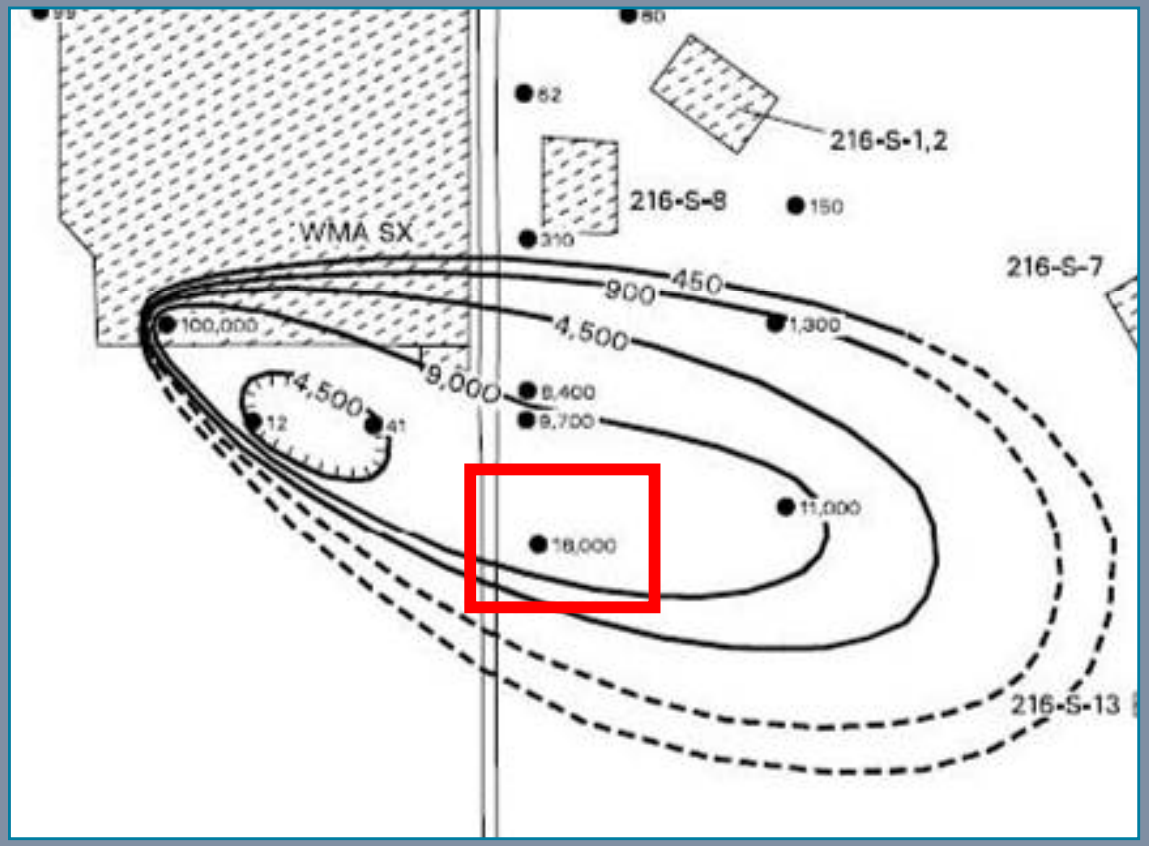
Average Technetium-99 Concentrations at Waste Management Area S-SX

Top of Unconfined Aquifer (PNNL-15670)





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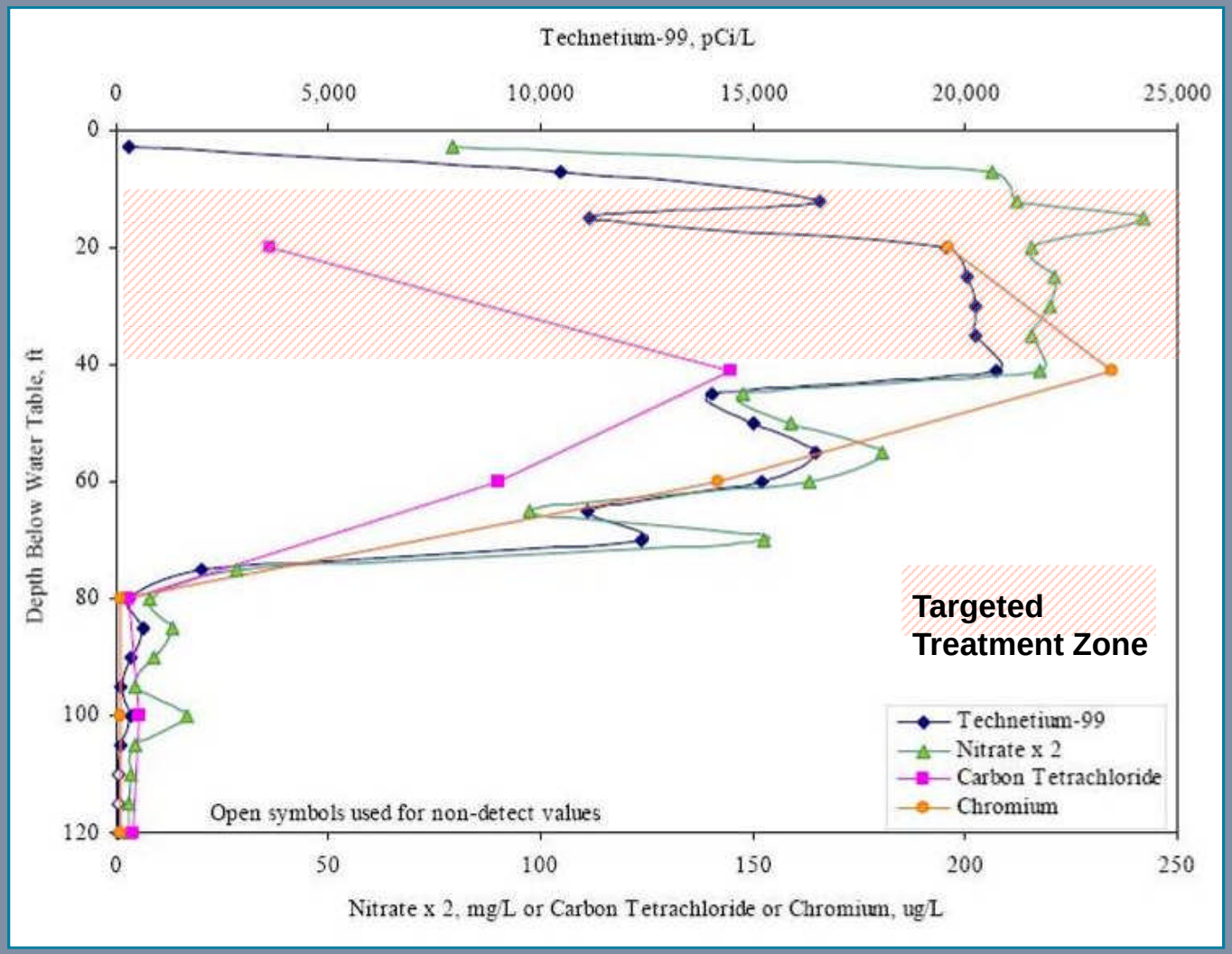
Concentration of Selected Analytes

Samples Collected during Drilling of Well 299-W22-47



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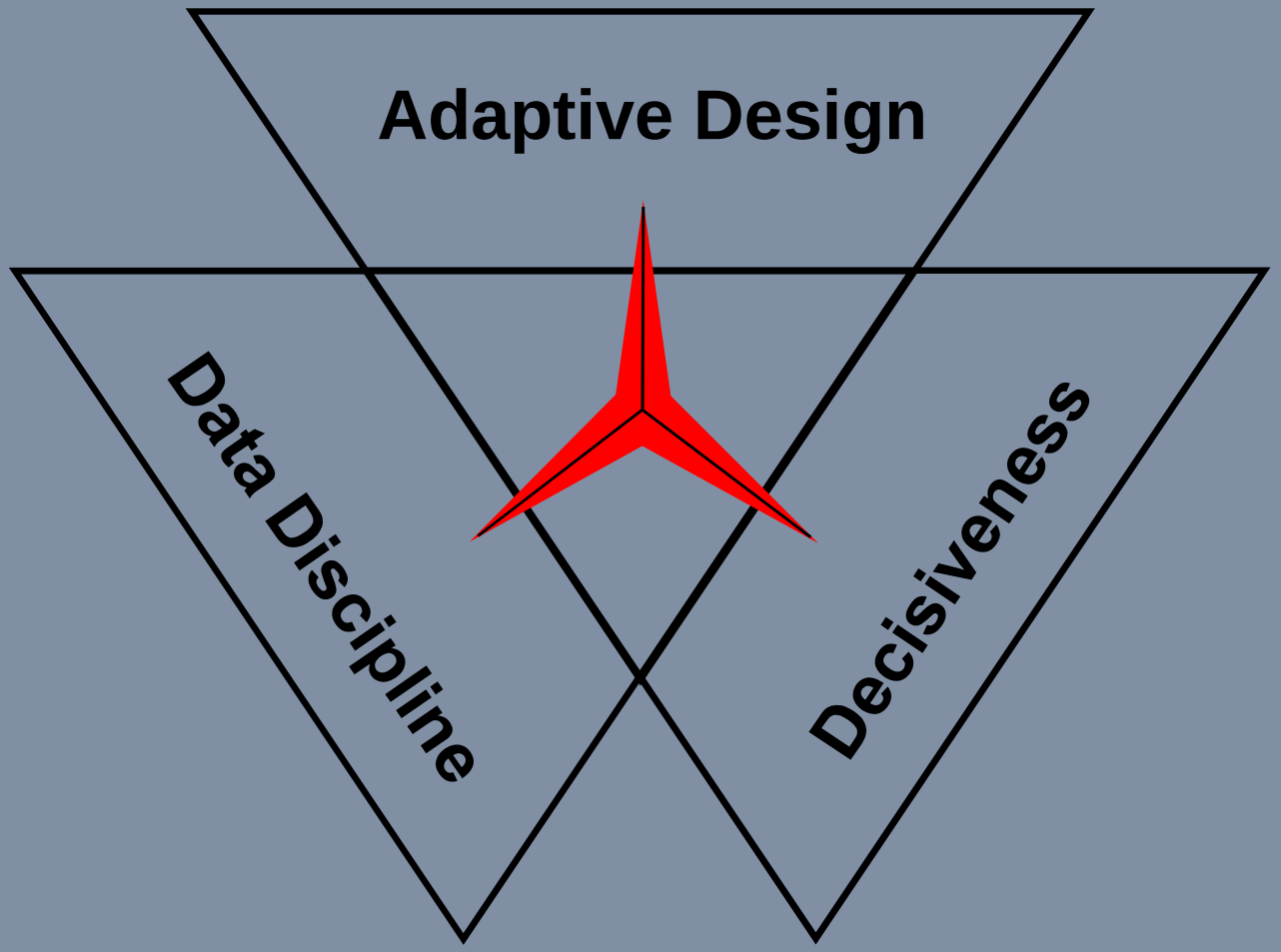
Three Elements of an Effective Remedial Strategy



Pilot Test Design Elements

- An initial PNNL bench scale test focused on site specific proof of concept and regulatory concerns
- Use one existing monitoring well (299-W22-47)
- Install three new injection wells and four monitoring wells to 70-80 m bgs with 10 m screens
- Air rotary drilling planned
- Drilling to be subcontracted through Fluor Hanford
- Total of 10 injections, initially monthly then quarterly

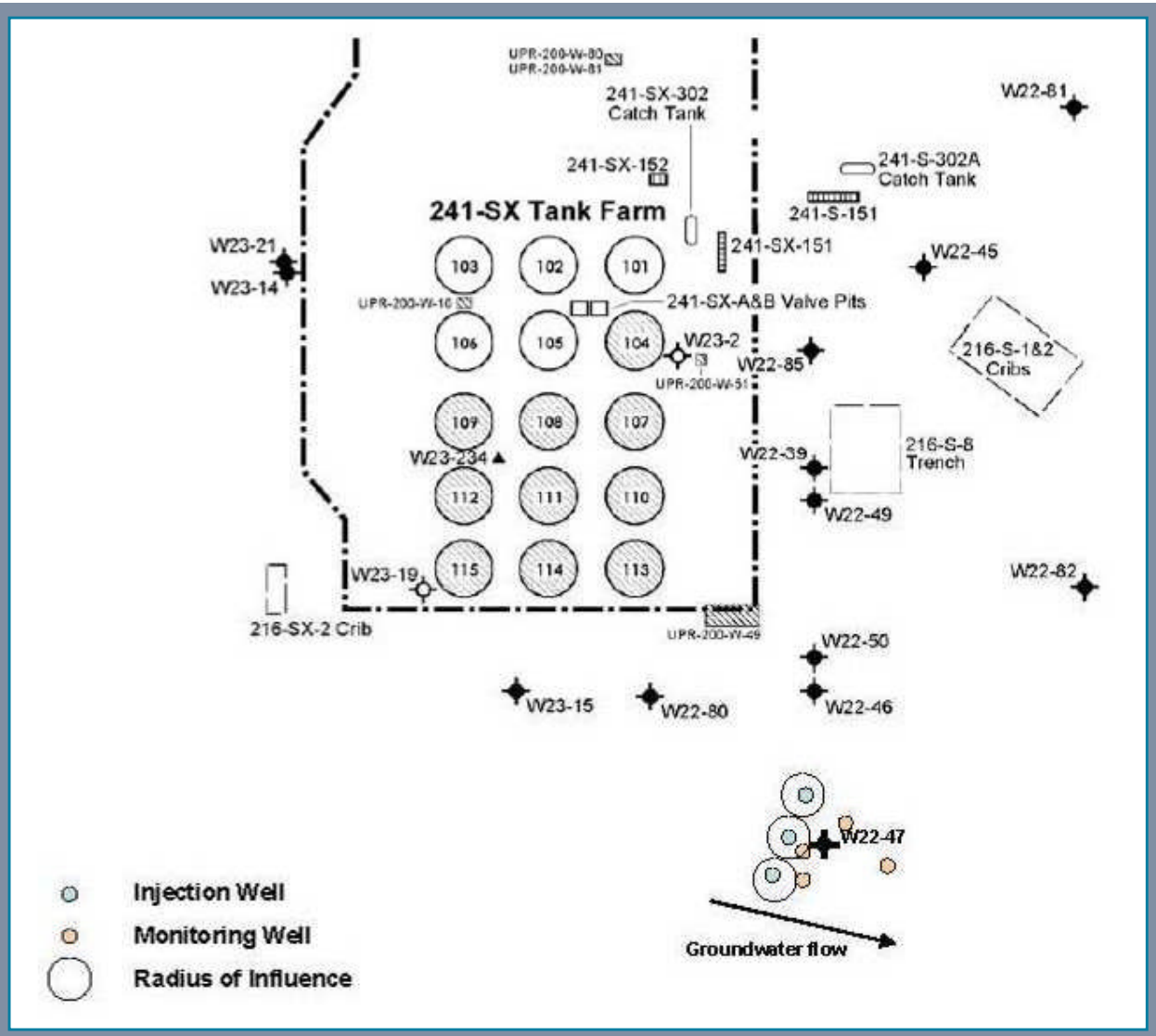
Pilot Test Design Elements
(continued)

- Soil sampling for speciation before and after treatment
- Molasses substrate, 20 day half life, 0.8% solution, 8,300 gallons per meter of screen
- Volume injected 83,000 gallons per well at 45 gpm, 31 hours of injection time
- Resulting in radius of influence 10 m and post dilution TOC in-situ of 1,100 mg/l
- Ferrous sulfate heptahydrate added to aid precipitation and prevent reoxidation

Logistics for Injection

- Mix water for the injected substrate will be obtained from an acceptable source. Sources could include: 1) 200 UP-1 pump and treat system; or 2) fire protection system.
- There is no on-site power source, generators will be needed
- The lithology within the proposed pilot test area is favorable for high volume (8,300 gallons per foot of screen) injections.
- A clean water flush will be used following the carbohydrate injection to prevent biofouling of wells in the IRZ

Pilot Test Location in S-SX Area



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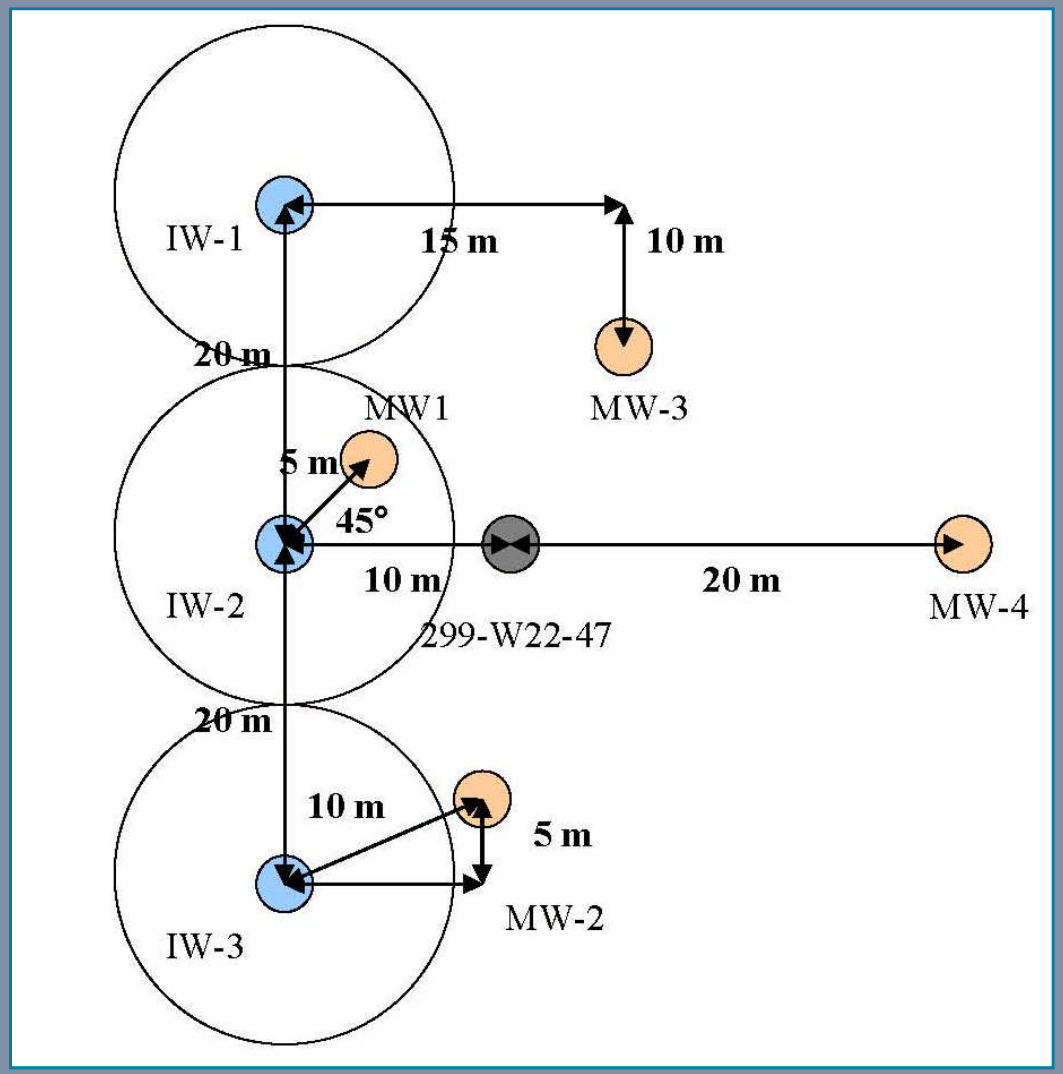
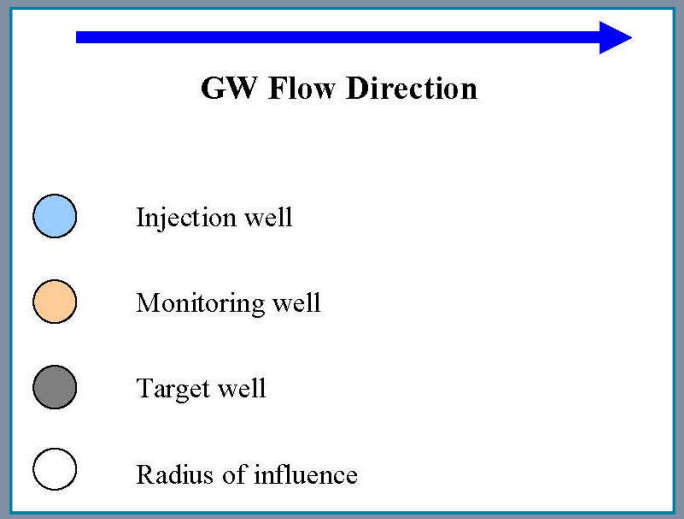
Conceptual Pilot Test Layout

Molasses as carbon substrate (figure not to scale)





Activities Preceding Pilot Test

- Phased well installation
  - For tracer test, install only two wells
- Bench scale test
- Tracer test
- Modeling/Design Calculations
  - Simulate EARP/denitrification approach

Bench Scale Study

- Proof of concept for Tc applications
  - using site-specific materials
  - not strictly necessary but may be needed for regulatory acceptance
    - available information in the literature
    - greater accuracy of field scale tests for this technology

Bench Scale Study
(continued)

- Partner with PNNL to execute, to minimize logistical and permitting issues
  - PNNL's mechanistic studies of biogeochemical processes controlling Tc fate and transport in aquifer sediments are relevant to ARCADIS field test
    - Fredrickson et al. 2004; Wildung et al. 2004; Zachara et al. 2006; Zachara et al. 2007, Fredrickson et al. 2007; and Peretyazhko et al. 2007
    - Current work: "Technetium and Iron Biogeochemistry in Suboxic Subsurface Environments with Emphasis on the Hanford Site" (started FY 2007), funded by DOE Office of Biological and Environmental Science, Environmental Remediation Sciences Program; examines processes related to Tc geochemistry in Ringold formation sediments from Hanford 200 Area

Bench Scale Study
(continued)

- Lab tests could be conducted in parallel with existing and planned research at PNNL
  - Using Tc biogeochemistry capabilities developed with BER support
  - Focus on Tc reduction/reoxidation and related changes in the sediment geochemistry/hydrology as a function of the type & concentration of proposed amendments (e.g., organic substrates to promote microbial reduction)
  - Include Tc reduction and then reoxidation in batch microcosms prepared with site-specific soil and groundwater
  - The batch results could then be verified and kinetics further determined with a 1-D column study

Tracer Test

- Objectives
  - Confirm groundwater flow direction
  - Determine mobile porosity, radius of influence
  - Refine optimal well placement, injectant volume & strength
  - Determine frequency of injection
- Use 3 wells
  - Install IW-1 as injection well
  - Install MW-1 as monitor well
  - Use existing well 299-W22-47 as monitor well
- Tracer to be determined – costed based on fluorescein dye

Planned Analytical Work

- Tracer studies
  - Quantitative tracer analysis
- Process Monitor Parameters (total of eleven rounds)
  - Key COC concentrations and chemistry (Tc, nitrate, Cr(VI))
  - Monitor EARP and denitrification performance – TOC, field parameters, gases, Fe (total and dissolved)
- Full Biogeochemical Monitoring Rounds (five rounds)
  - All of the parameters from the process monitoring suite
  - Plus RCRA metals, cations, VFAs, DOC
- Solid-phase analyses
  - Quantify reactive mineral phases
  - Identify sorbed COCs
  - Iron and manganese forms

Standard Performance Monitoring Analyses

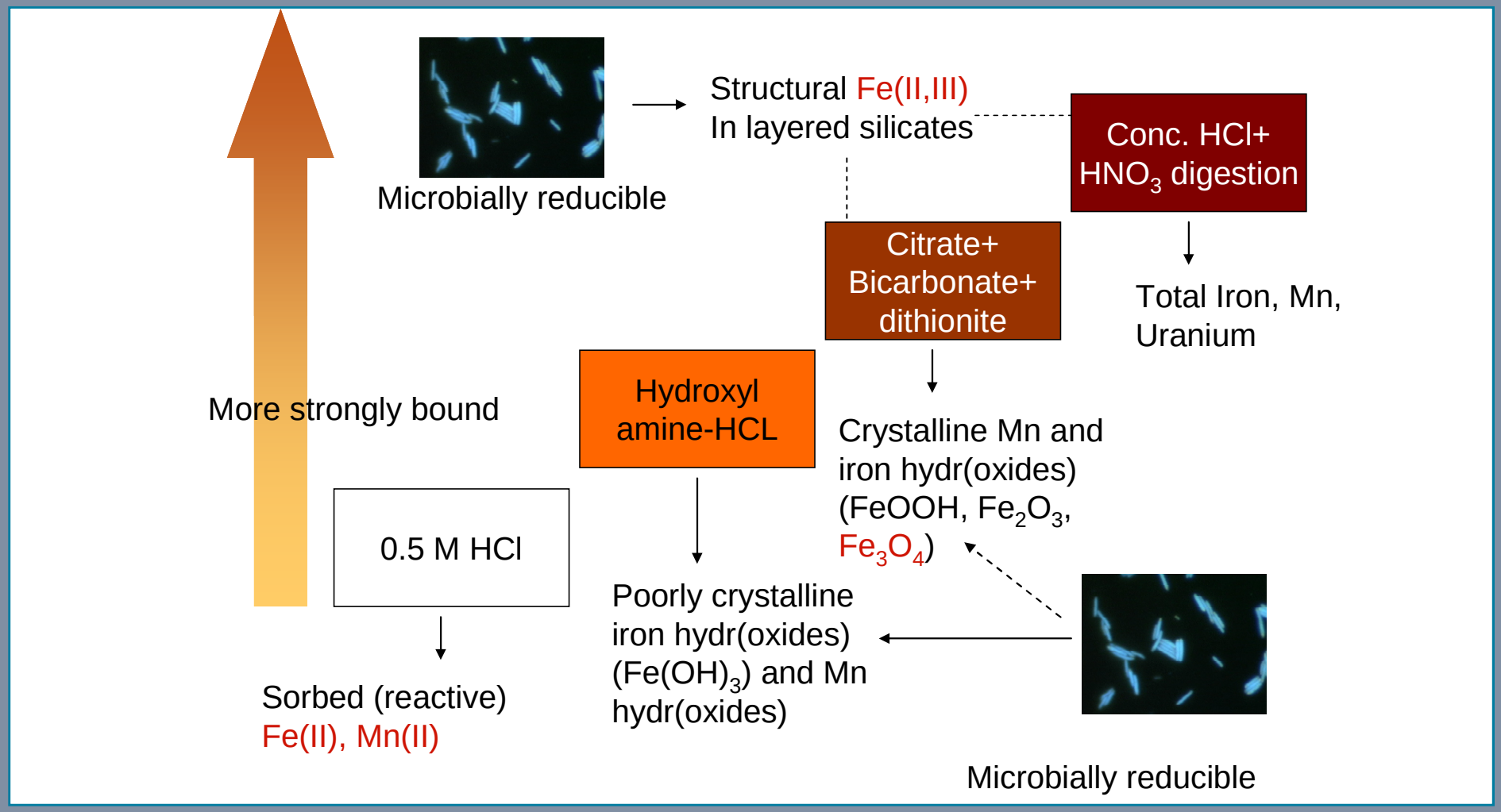
Field and Lab Parameters – Groundwater Samples

- Field
  - Temperature, pH, ORP, DO, Specific Conductance
- Lab
  - U, Tc
  - TOC, Anions (NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, Cl^-), Iron (total and dissolved), Al, S^{2-},, CO_2, CH_4
  - Cr(VI), Cr_T, CAHs as applicable
  - Microbial populations by DGGE and PLFA
  - Analyses performed by certified labs capable of handling radioactive samples

Advanced Speciation Methods for Solid-phase Samples

- X-ray diffraction
  - to identify mineralogy of ***reactive species*** (mixed-valent iron and iron sulfides) formed in IRZ and immobilized U phases
- Scanning electron microscopy/energy dispersive spectroscopy
  - to identify ***reactive minerals*** and COC-elemental association
- X-ray absorption spectroscopy
  - to verify creation of ***reduced*** U, Tc, Cr species (XANES); to identify elemental association of reduced COCs (μXRF, μXRD).

Selective Extraction of Fe, Mn, U from Aquifer Solids



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Quality Assurance

- DO EM QAPP Basis:

  10 CFR 830 & DOE Order 414.1C
- DOE EM QAPP Components:

  10 Criteria for Quality Assurance
- DOE in Tri-Party Agreement with:

  Washington Department of Ecology

  U.S. Environmental Protection Agency

Imagine the result

Appendix
Supplemental Slides

Radionuclide Experience

Maintenance Shop Area Site, TN (Confidential DoD and DOE Contractor)

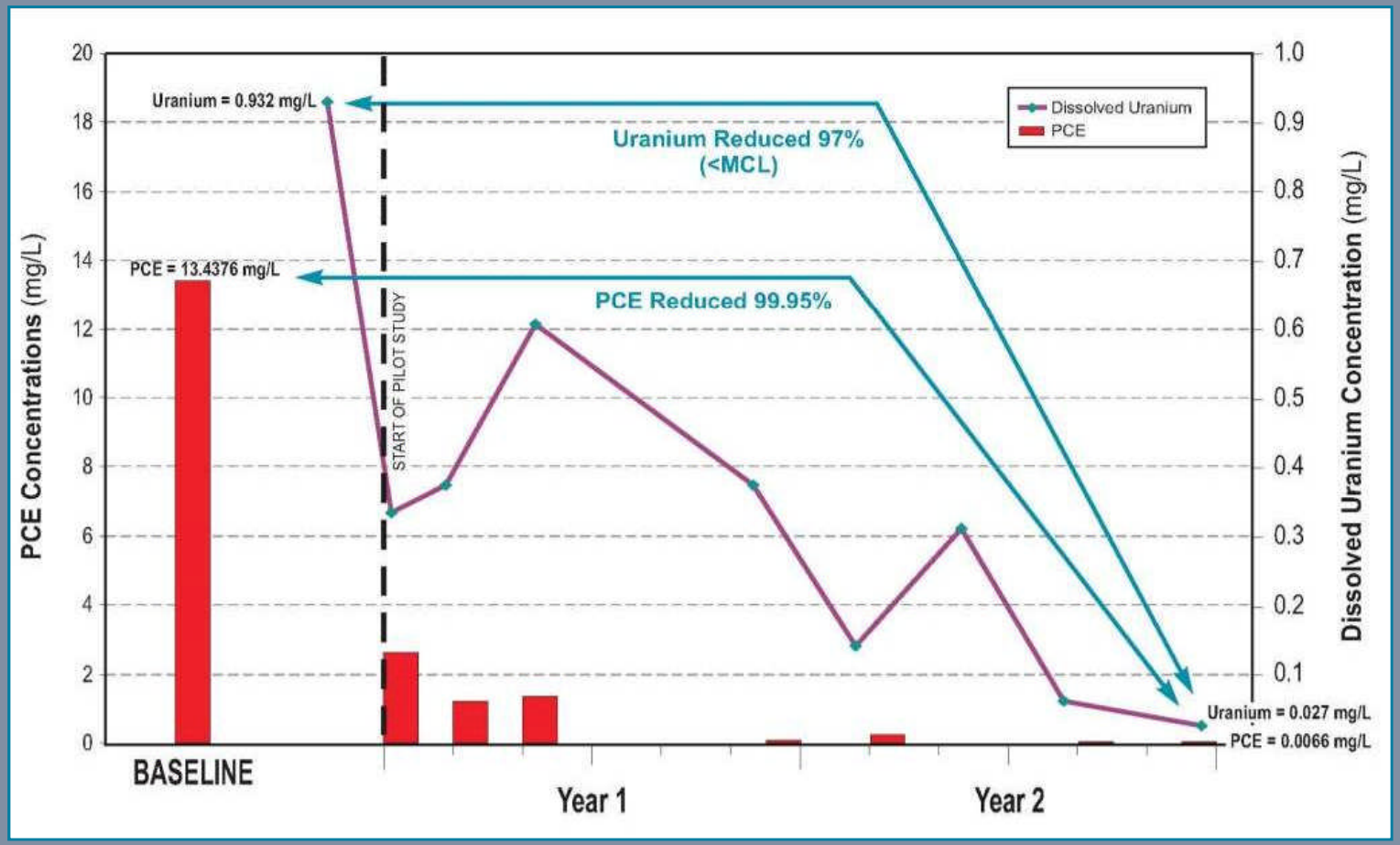
- Identified, evaluated and screened remedial alternatives to:
  - Prevent further migration
  - Enhance the degradation of CAHs
  - Remediate dissolved uranium
- Selected Enhanced Anaerobic Bioremediation and Reductive Precipitation for dissolved VOCs, PCE daughter products, U, and TBP

Radionuclide Experience

Maintenance Shop Area Site, TN (Continued)

- Data from the IRZ pilot study has been positive
  - Initiated reagent injections in August 2000. Biogeochemical data indicate the reactive zone was established.
  - Pilot study (September through November 2000) show concentrations of both total and dissolved uranium (U234, U235, and U238) have been reduced > 50%.
  - Concentrations of other inorganic constituents (chloride) have remained stable, supporting the conclusion that reductions in the U concentrations are due to in situ precipitation of the metals.
- Project featured by EPA as “RCRA Cleanup Reform Success Story”

Successful Clean Up of Mixed Uranium and PCE Plume



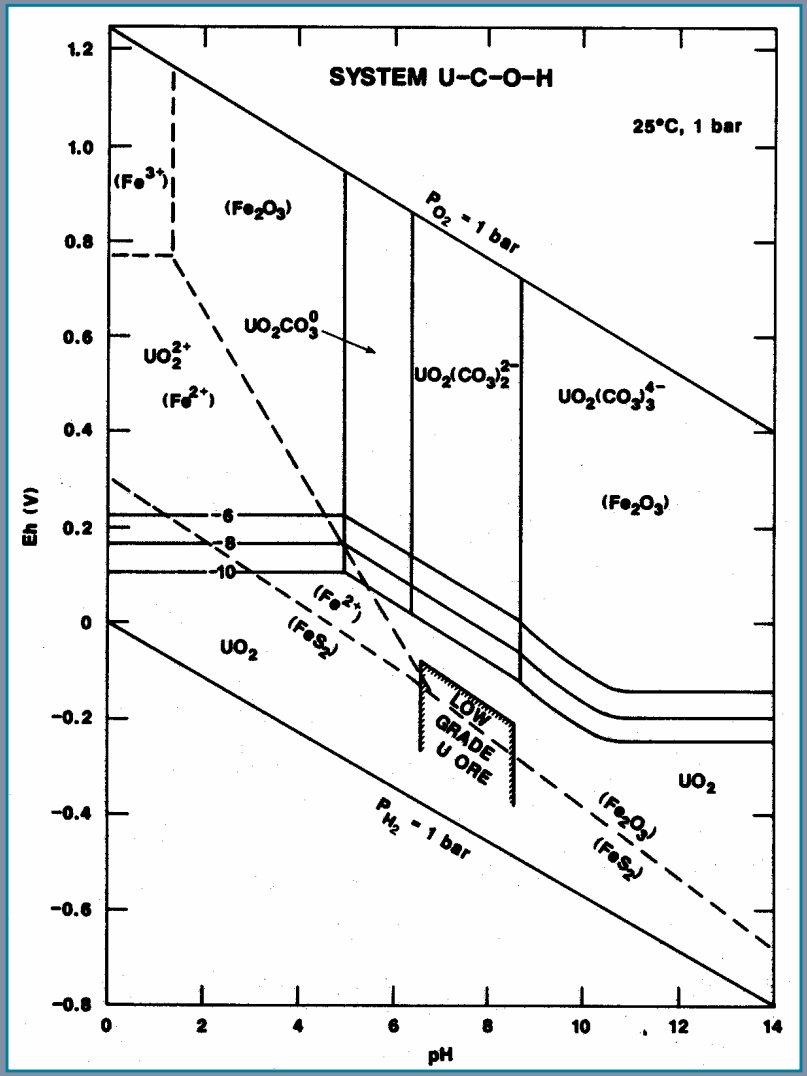
Uranium Treatment Mechanism

- Under ordinary aerobic conditions, uranium exists is the +6 state.
- When we reduce the Eh, the mixed oxide, U_3O_8, is established over a fairly narrow Eh-pH range and then uranium is reduced to the +4 oxidation state and the solid oxide, UO_2, is the stable species.
- In the presence of naturally occurring iron and reduced sulfur, co-precipitation will occur with pyrite.

Uranium Treatment Mechanism
(continued)

- UO_2 is the naturally occurring mineral uraninite, the pure uranium mineral found in pitchblende. Thus, it can be expected to remain stable.
- When Si is a significant species, there is an immobile mineral form, coffinite ($USiO_4$) that has a large stability field under reducing conditions.

Eh-pH Diagram for the U-C-O-H System with Iron Present



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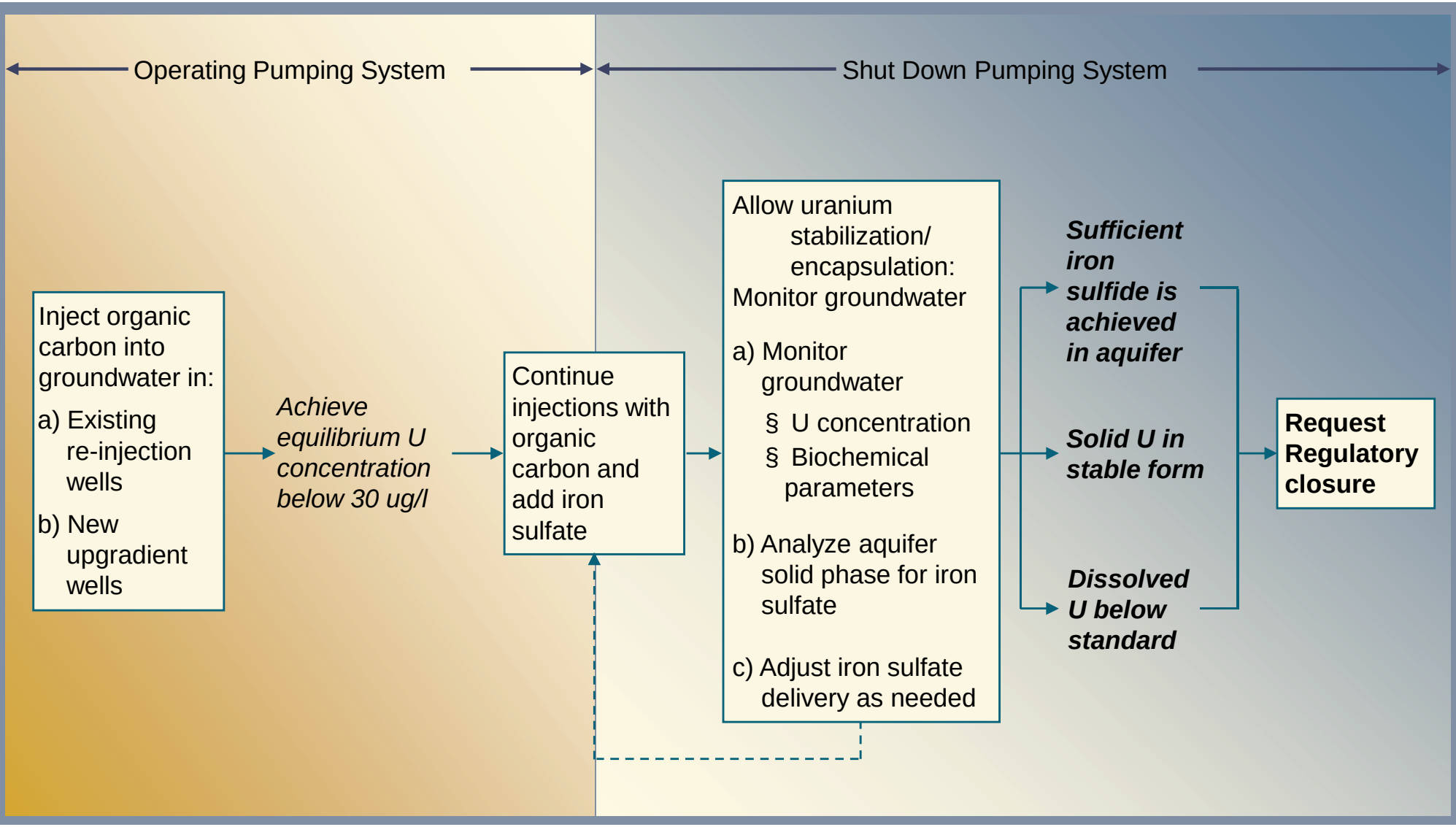
Conceptual Implementation of ARCADIS Technology at a Site with Existing Uranium Pump and Treat



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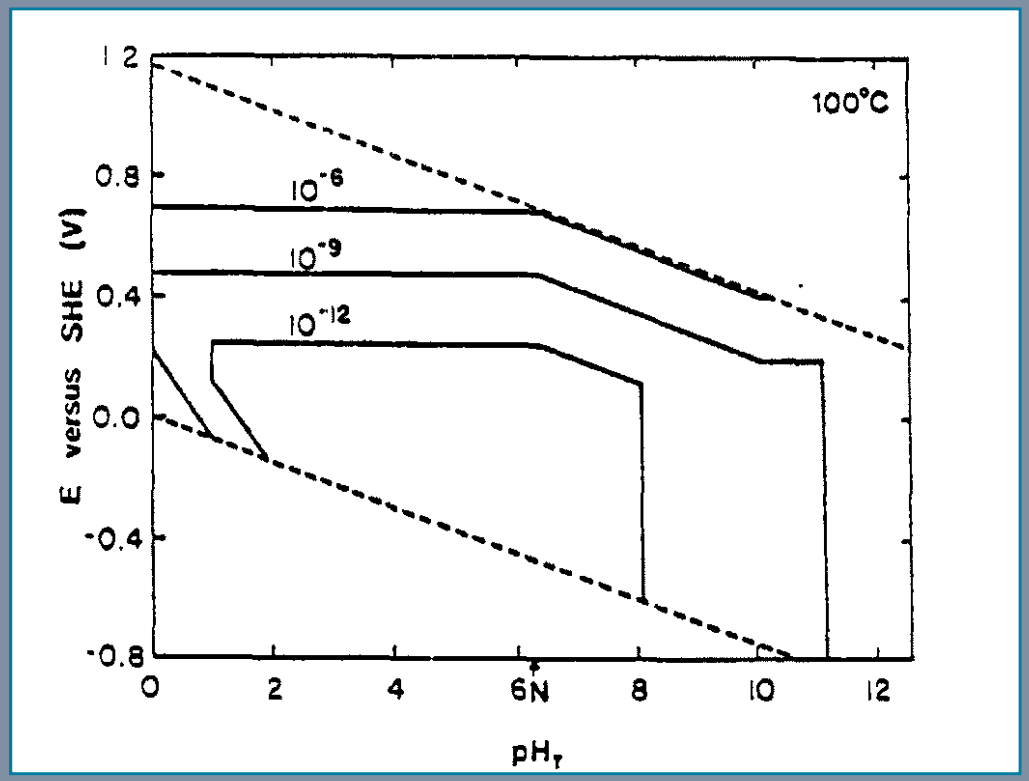
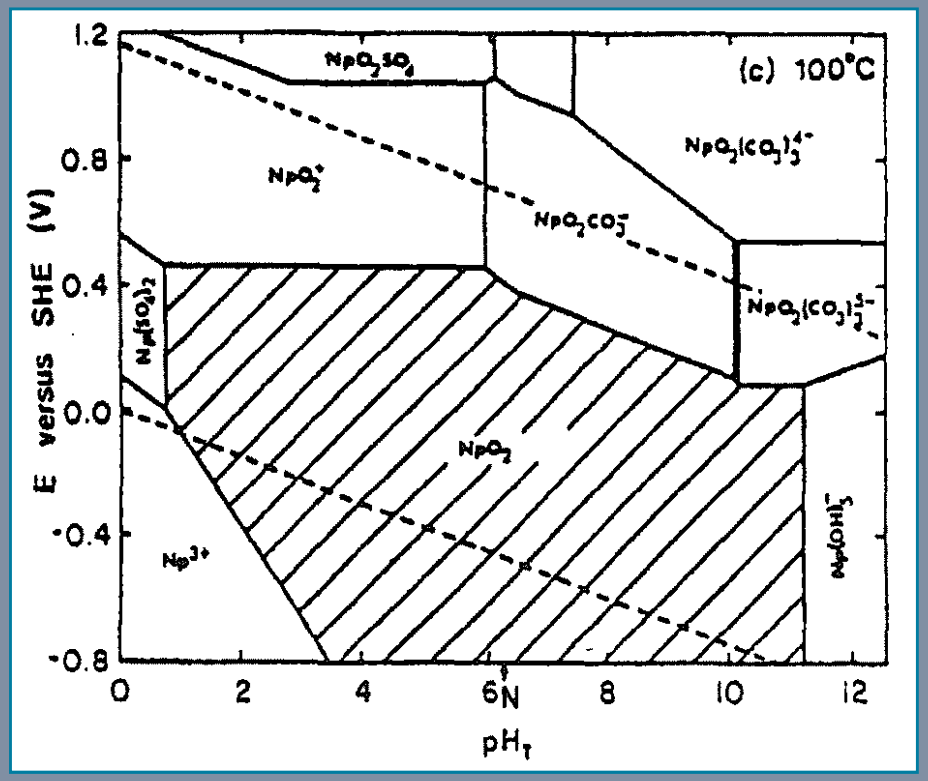
Eh-pH Diagrams and Stability Contours for Np





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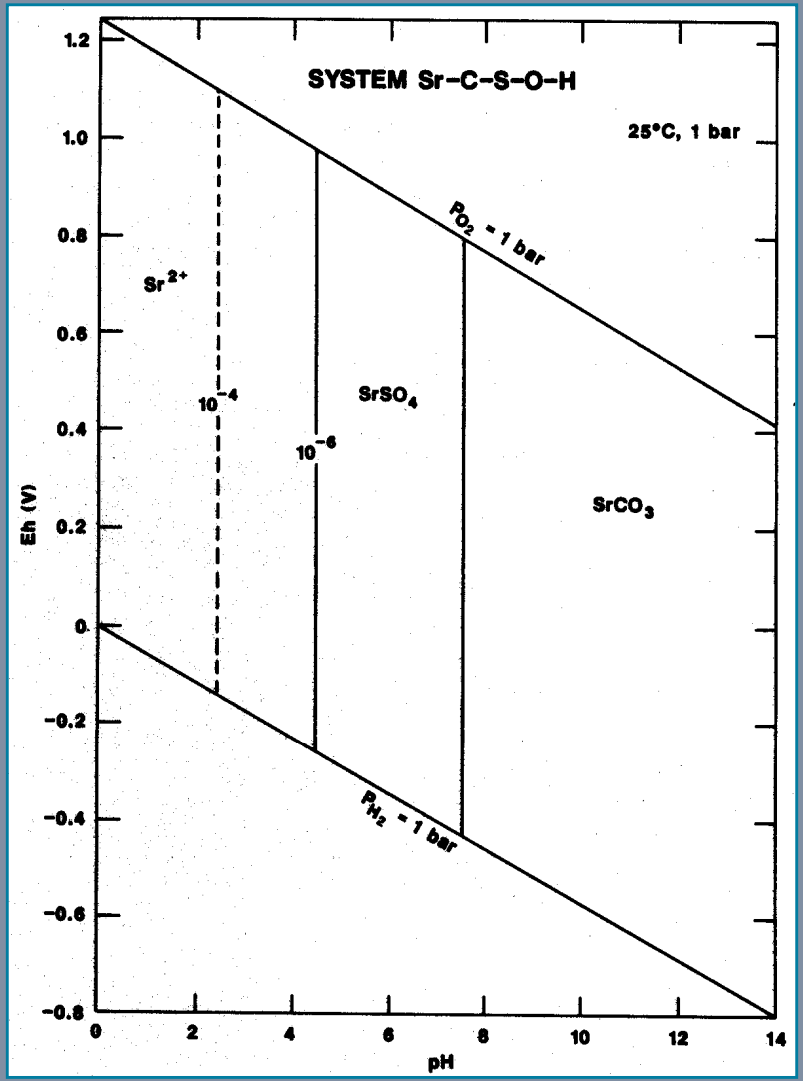
Stabilization of Aqueous Strontium-90



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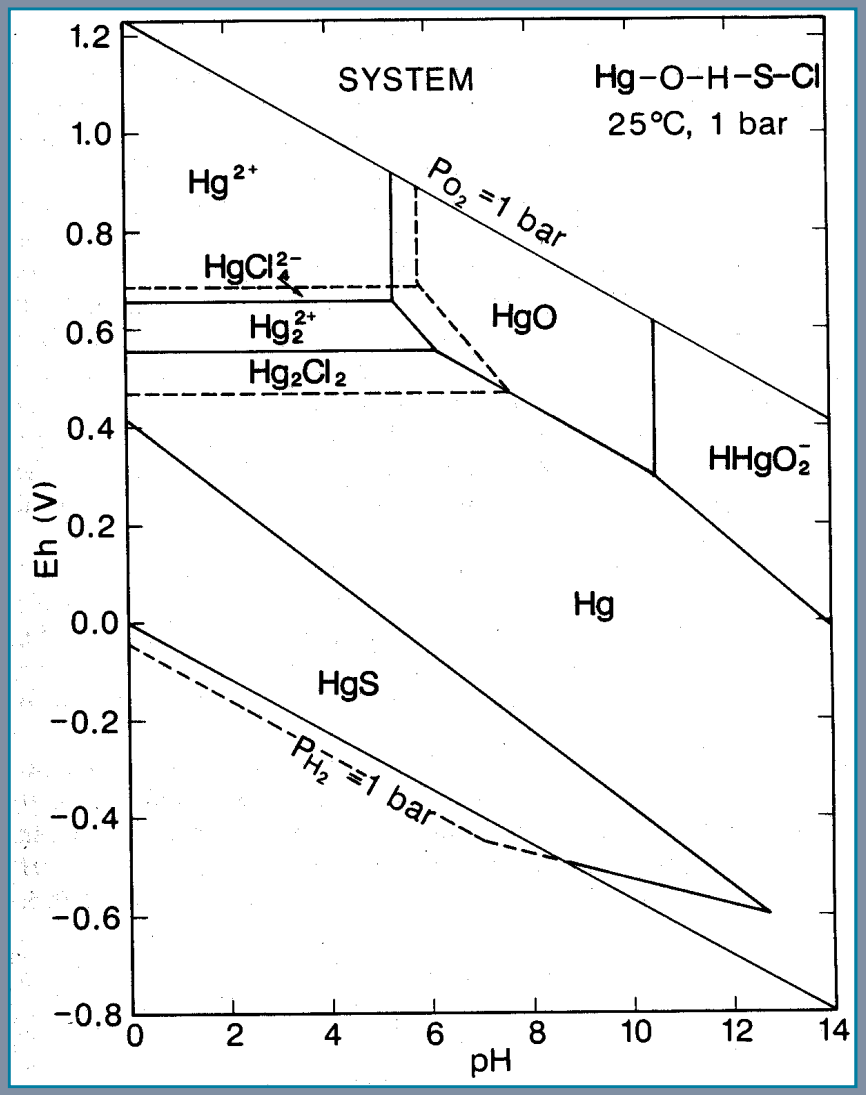
Eh-pH Diagram for the System Hg-O-H-S-Cl



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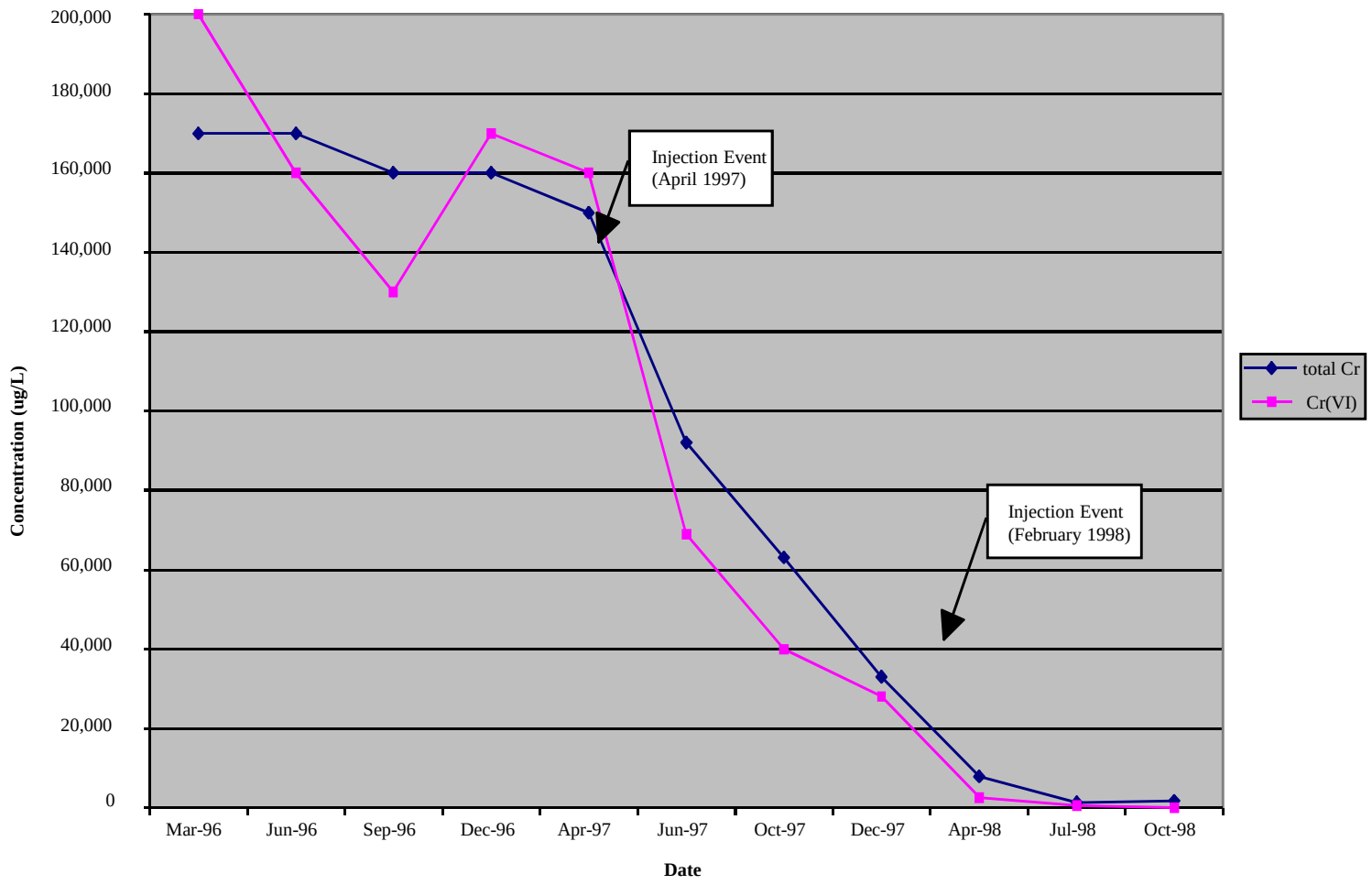
Analytical Results, Well MW-13
Abandoned Manufacturing Facility, California



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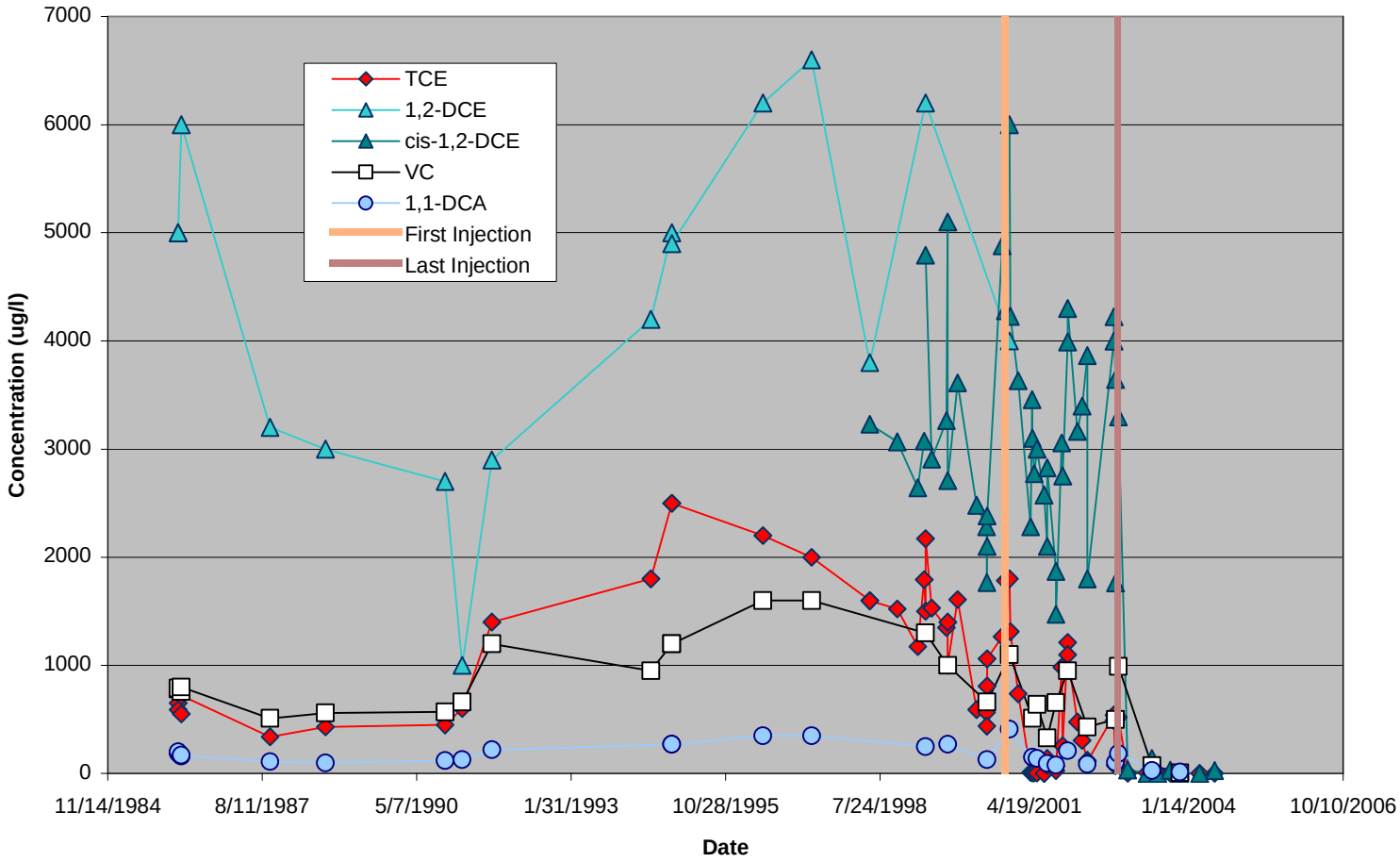
CAH Source Zone Applications

- Hanscom Air Force Base Demonstration
  - Pilot test wells identified contaminant distributions indicative of a source area
  - Though no DNAPL found, groundwater model (CH2MHill) required a source in this area to simulate CAH distributions
  - ESTCP/AFCEE Project

Source Zone Application - HAFB



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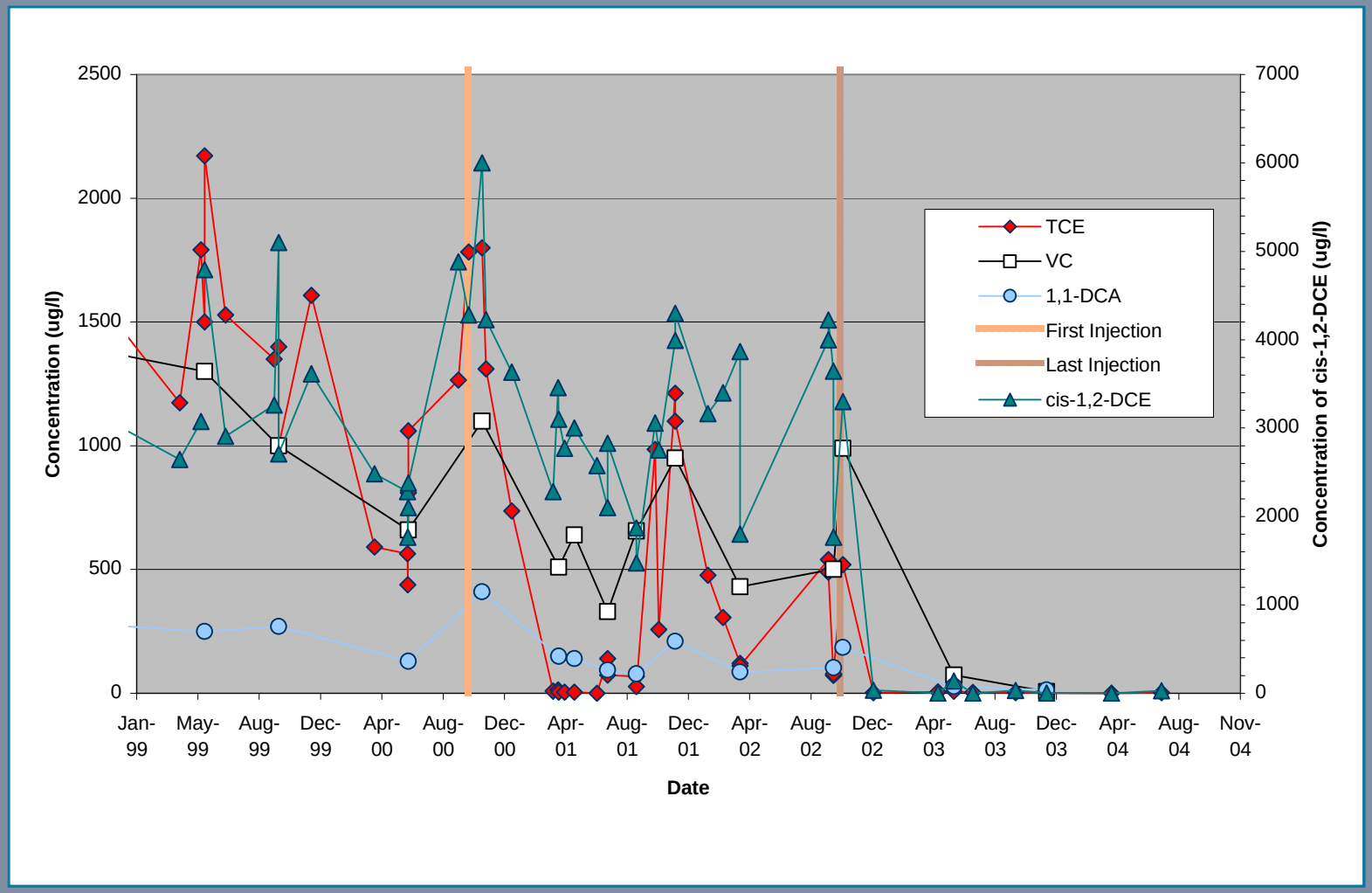
Source Zone Application - HAFB



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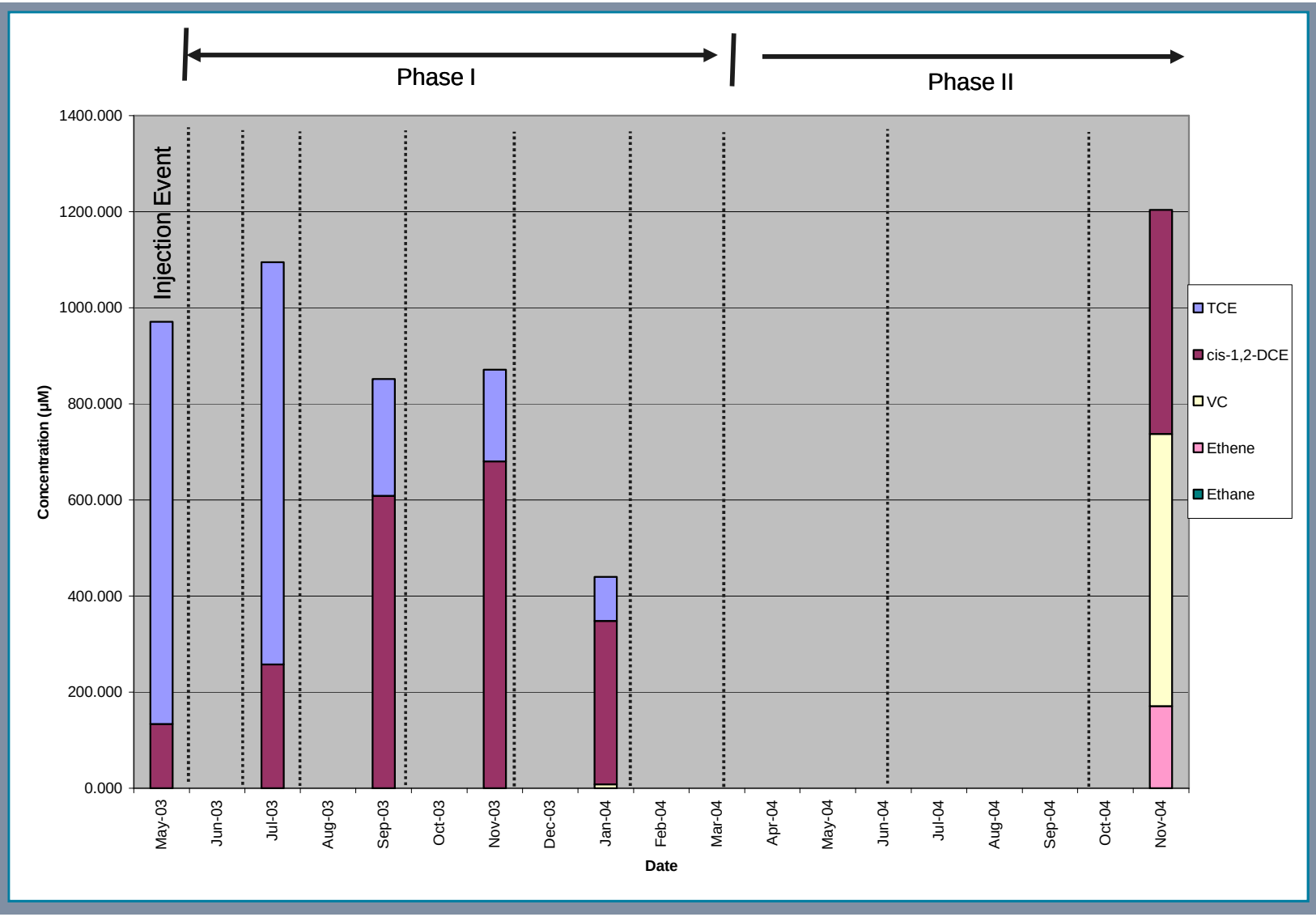
CAH Source Zone Applications

- Charleston Air Force Base
  - Concentrations of TCE have ranged as high as 296 ppm, indicating the presence of NAPL and/or sorbed-phase mass
  - Guaranteed fixed priced remediation project

MW88-15 Deep Source Zone Mass Balance - CAFB



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Continued Technology Refinement

- Emphasis on hydrogeological characterization with tracer tests for distribution
- Large volume injections of dilute reagent
- Very focused monitoring data sets for CAHs, performance indicators
- Look for mining of source/sorbed material
- Realistic expectations about time frames

Tc Treatment Mechanism

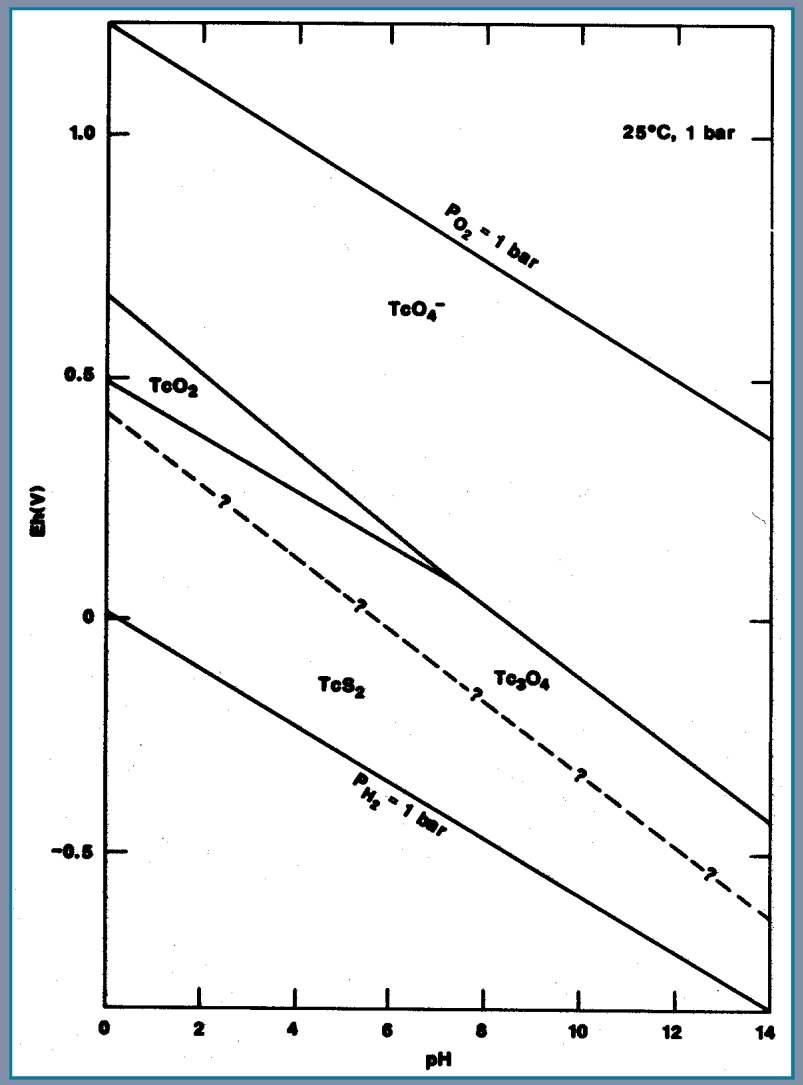
- The anion TcO_4^- is the stable species under ordinary aerobic conditions. As EARP technology is implemented, this ion is reduced;
  - First to TcO_2
  - Then to the mixed oxidation state oxide, Tc_3O_4 or the hydroxide $Tc(OH)_2$
  - Finally, as reductive conditions stabilize and sulfides are generated the stable compound TcS_2 becomes the dominant species

Brookins: "The stability of the TcS_2 species is well documented under sulfur-present conditions in laboratory experiments."

Tc Treatment Mechanism (continued)

- Lee, 1983: "Pertechnetate oxyanion….was removed from a brine solution by precipitation with sulfide, iron and ferrous sulfide at environmental pH's…..the black precipitate obtained from the TcO_4^- sulfide reaction was poorly crystallized technetium sulfide (Tc_2S_7) which was insoluble in both acid and alkaline solution in the absence of strong oxidants"
- Lemire, 1996: "It is probable that Tc(IV) oxides are more stable than previously predicted and, hence they are less likely to be oxidized to TcO_4^- (aq) under moderately reducing conditions."

Eh-pH Diagram for the System Tc-S-O-H



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Technetium Radiochemistry

- First artificial element (^{96}Mo, 2n → ^{99}Tc)
- No stable isotopes
- Long-lived fission product of ^{235}U

Radioactive Properties of Key Technetium Isotopes

Isotope	Half-Life (*yr*)	Specific Activity (*Ci/g*)	Decay Mode	Radiation Energy (*MeV*)		
				Alpha (*α*)	Beta (*β*)	Gamma (*γ*)
Tc-97	2.6 million	0.0014	EC	-	0.0056	0.011
Tc-98	4.2 million	0.00088	β	-	0.16	1.4
Tc-99	210,000	0.017	β	-	0.10	-

EC = electron capture, Ci = curie, g = gram, and MeV = million electron volts; a dash means the entry is not applicable. (See the companion fact sheet on Radioactive Properties, Internal Distribution, and Risk Coefficients for an explanation of terms and interpretation of radiation energies.) Values are given to two significant figures.

^{99}Tc = 17×10^9 pCi/g
1mg = 17μCi

at Hanford 200S-SX-1;
max conc. Is 20,740 pCi/L

1.2 μg/L

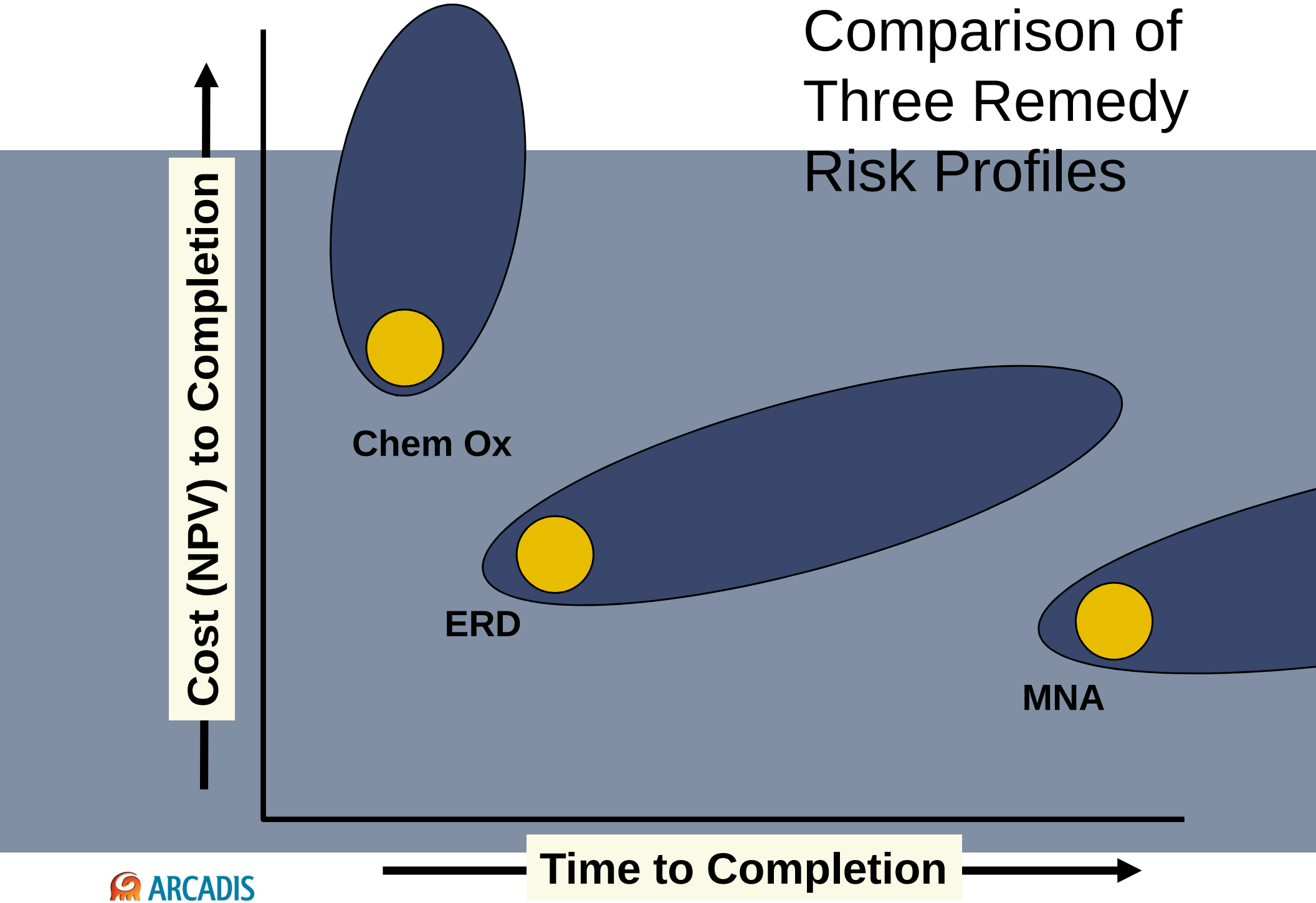
Hydraulic Conductivity – Sources

- The K range 0.02 to 61 m/day (0.06 to 200 ft/day) given on previous slides is from the 1994 RI/FS for the 200-UP-1 area. Backup/source undetermined.
- There's 2000-2001 data available from known wells/screened intervals in the S-SX area. Here's a rundown that focuses in on increasingly specific K ranges:
  - 0.58 to 17.2 m/d (PNNL 13514 and PNNL 14113, from slug tests and a few constant-rate pumping tests)
  - 0.78 to 5.7 m/d (a subset of the same data, looking at the 4-5 tests closest to the pilot test well & with comparable screened intervals to the pilot test)
  - 0.78 to 1.45 m/d (an even finer subset, 2 close wells with about the same screened interval as the pilot test)
- We are using the middle range for now, and looking for the additional data, especially for 299-W22-47
- The K range of 0.58 to 17.2 m/d generally corresponds to silty sand to clean sand

Velocity Information - Sources

- "Estimates of groundwater flow velocity, using travel times for tritium and technetium-99 between monitoring wells in the vicinity of Waste Management Area S-SX, suggest groundwater flow rates of 25 to 50 meters/year, or 0.07 to 0.14 meter/day" (PNNL-15670 - Hanford Site Groundwater Monitoring for Fiscal Year 2005)
- The next sentence in the same report says: "Calculated average linear velocities (using Darcy's method) based on hydraulic conductivity and tracer test data, also suggest similar flow rates (0.009 to 0.36 meter/day; see Appendix B)."
- Appendix B data confirms that the travel time estimate is in the same general area as our pilot test (will have to confirm the aquifer interval but probably about the same). The calculated velocities are based on 2000-2001 aquifer tests summarized below.
- These two are in good agreement

Comparison of Three Remedy Risk Profiles



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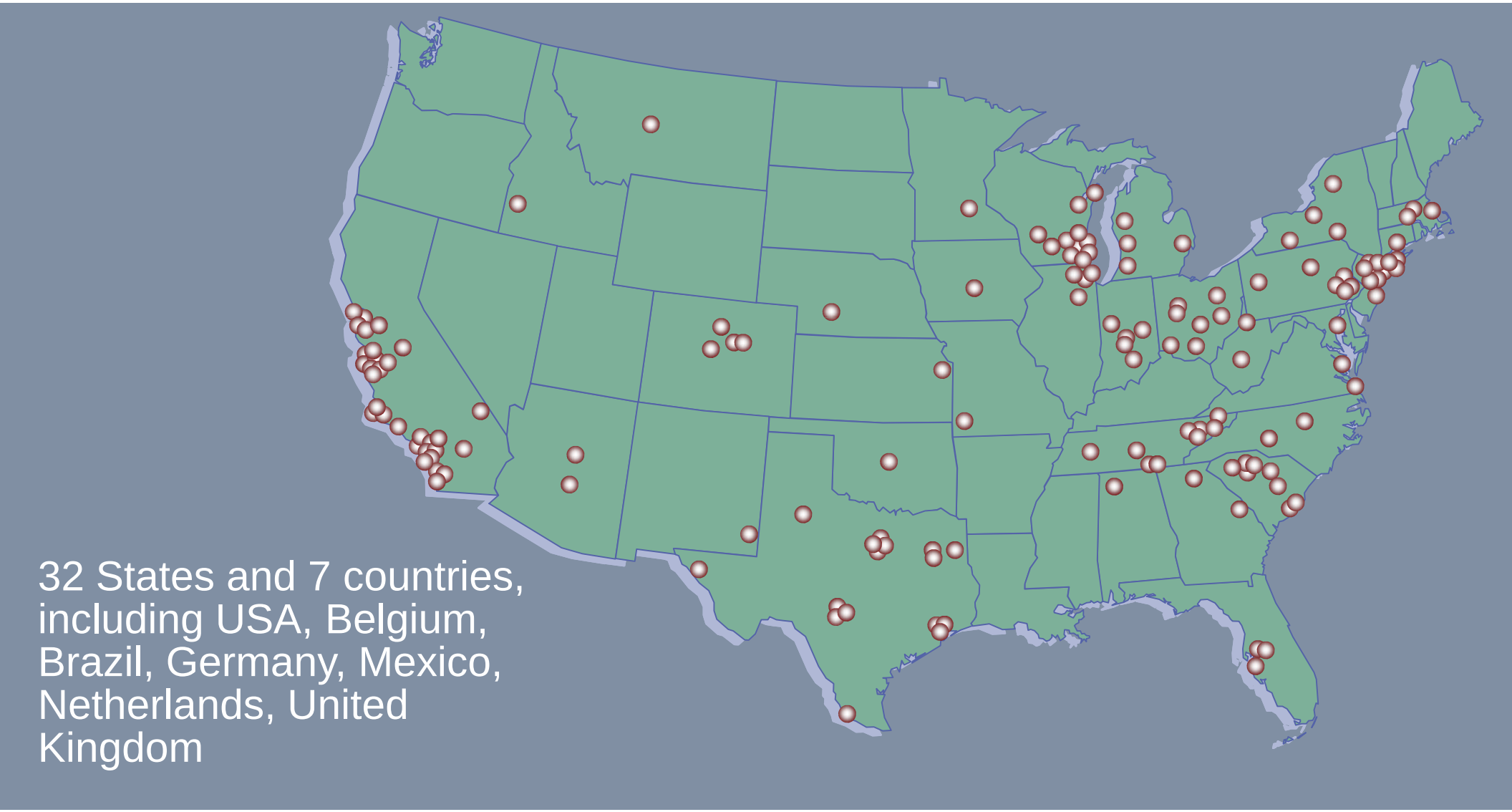
Carbohydrate Types Used

Category	Number of Sites
CAH Sites – Substrate information	112
Molasses	93
High Fructose Corn Syrup (HFCS)	3
Cheese whey	3
Molasses/HFCS	1
Molasses/whey	7
HFCS/whey	1
Molasses/CO2	4
Other	1

ARCADIS IRZ Applications in the U.S.



32 States and 7 countries, including USA, Belgium, Brazil, Germany, Mexico, Netherlands, United Kingdom

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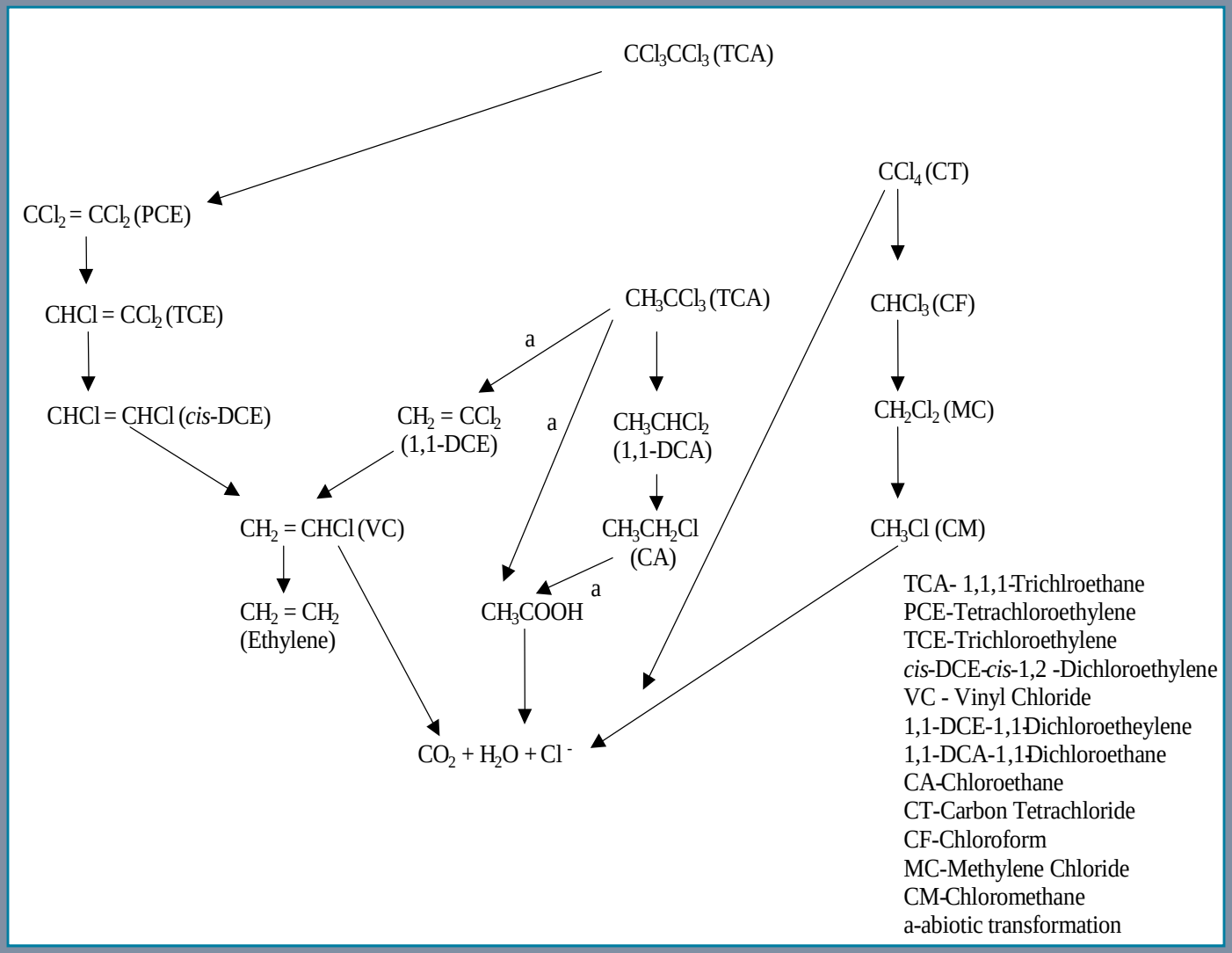
Breakdown Products Which Result from Reductive Dechlorination of CAHs



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