Fate and Transport of Radionuclides Beneath the Hanford Tank Farms: Unravelling Coupled Geochemical and Hydrologic Processes in the Vadose Zone

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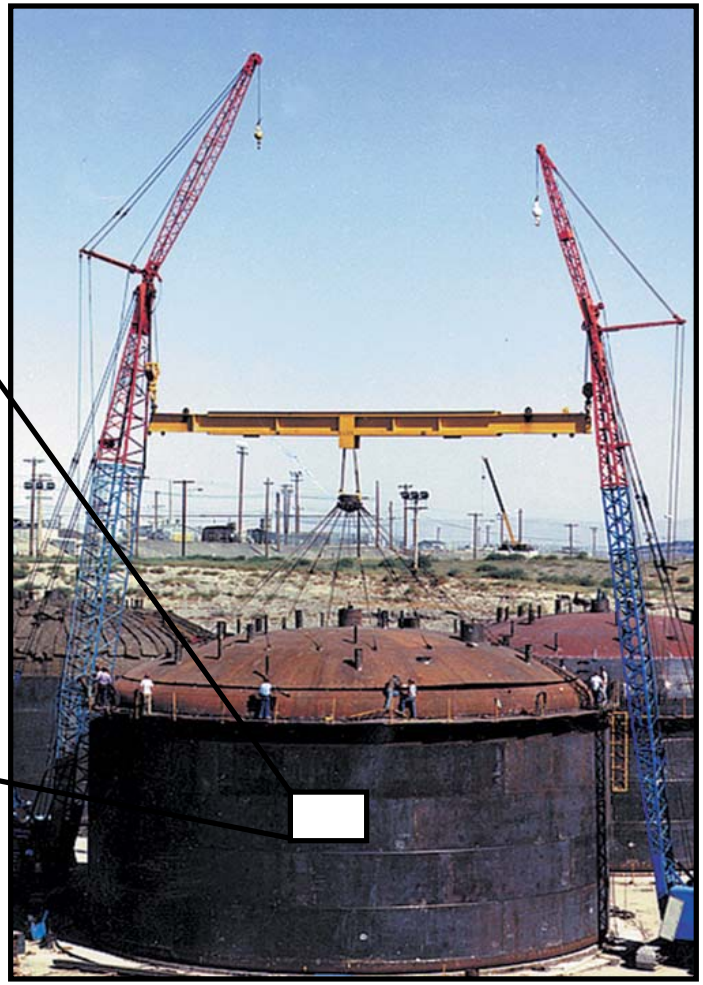
UT-BATTELLE

Goals



Provide conceptual and quantitative information on far-field contaminant transport rates and mechanisms in the Hanford vadose zone.

Objectives

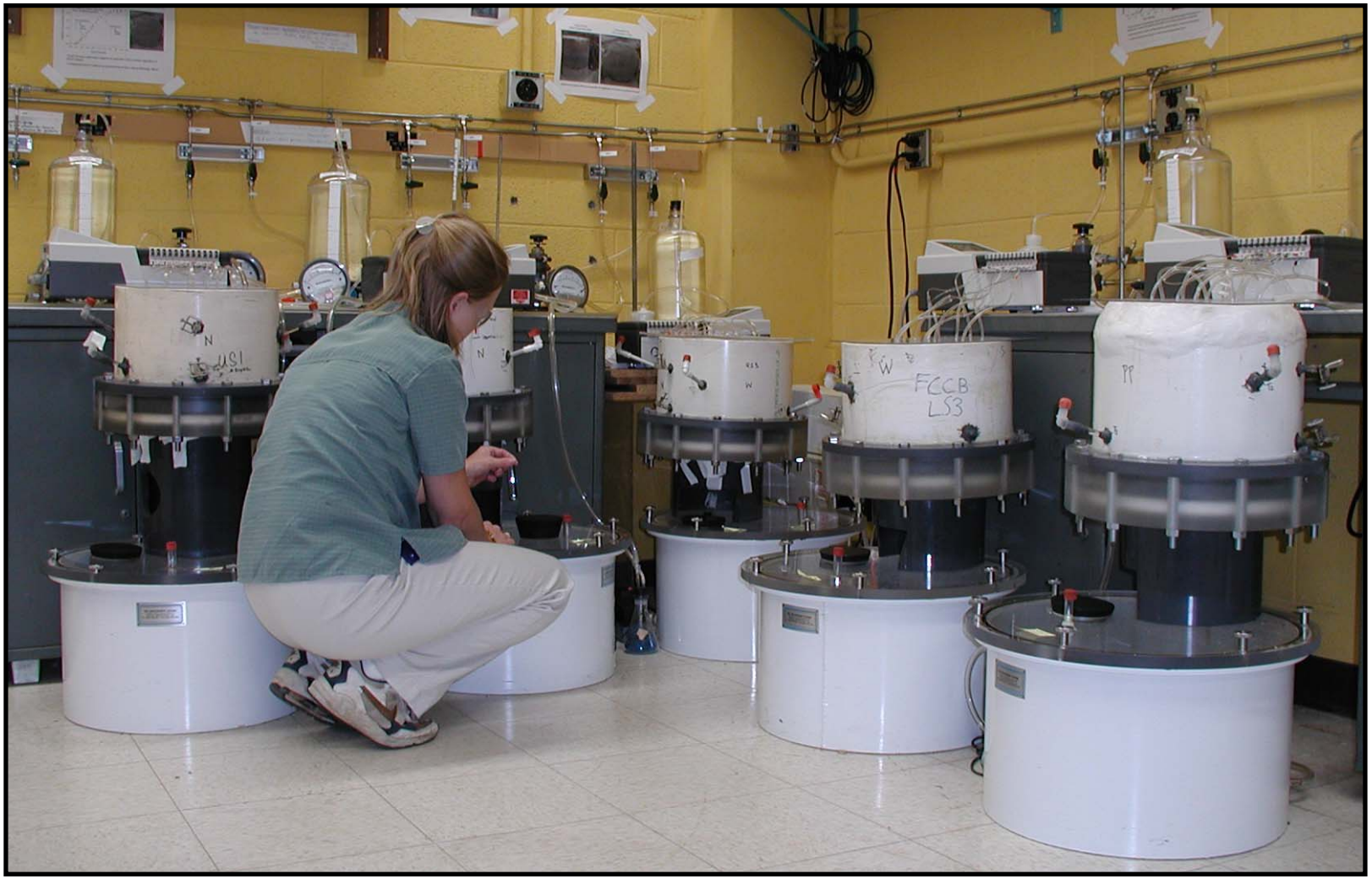
- Quantify hydrologic transport as a function of water content
  - Preferential flow, immobile water, matrix diffusion
- Quantify the rates and mechanisms of contaminant – sediment interactions
  - Adsorption, oxidation/reduction, chelate-contaminant dissociation, precipitation
- Quantify coupled hydrologic and geochemical processes
  - Isolation of hydrologic flowpaths to distinct sedimentary mineralogies as water content decreases

Approach

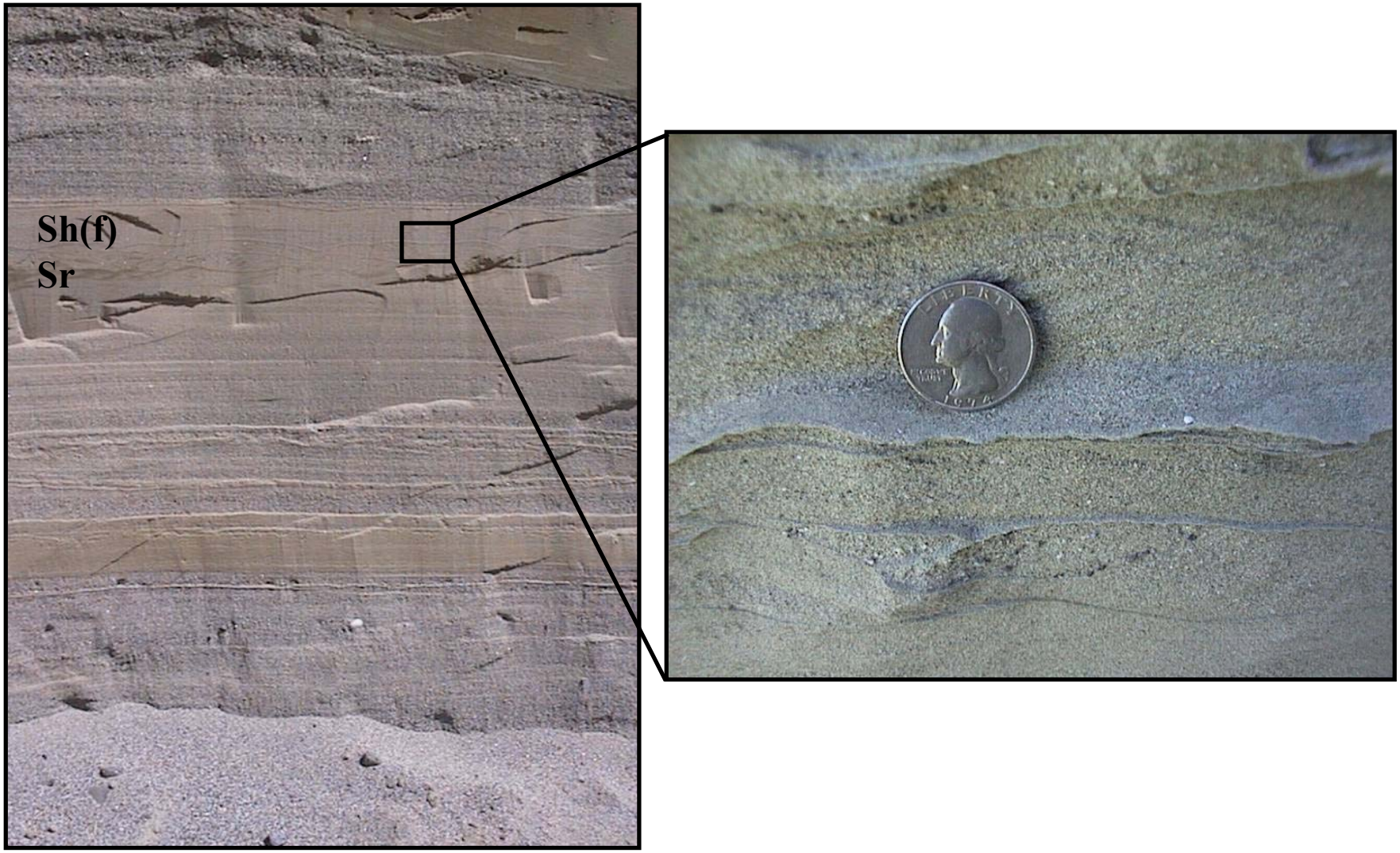
- Hydrology
  - Intact sediment cores
  - Lithologic heterogeneities and sedimentary features
  - Variable water content
- Geochemistry: Co(II)EDTA^{2-}, U(VI), Sr, Cs, Cr(VI)
  - High resolution surface spectroscopic techniques
  - Equilibrium and kinetic adsorption isotherms, miscible displacement
- Coupled processes
  - Unsaturated reactive transport experiments in intact cores
  - Long-term and quantitative (months, years)

Collection of undisturbed cores

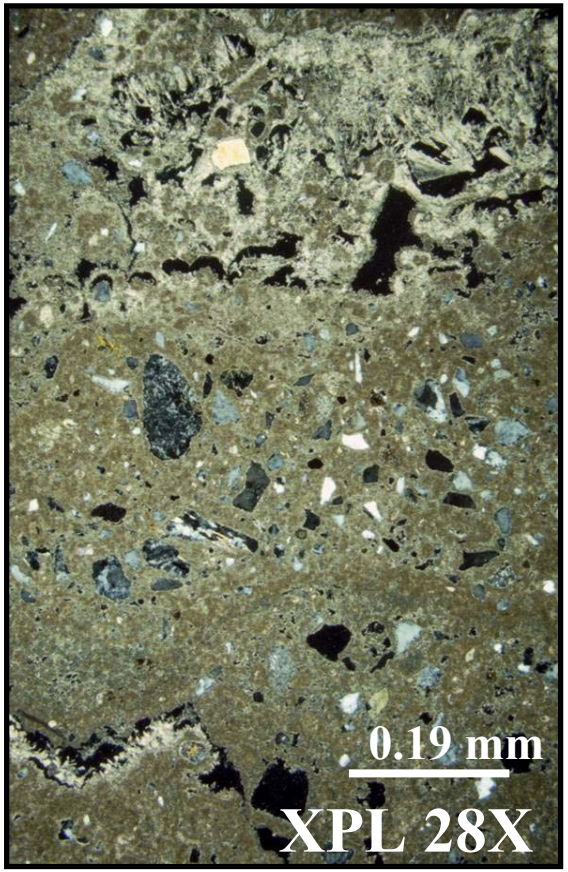
Experimental apparatus

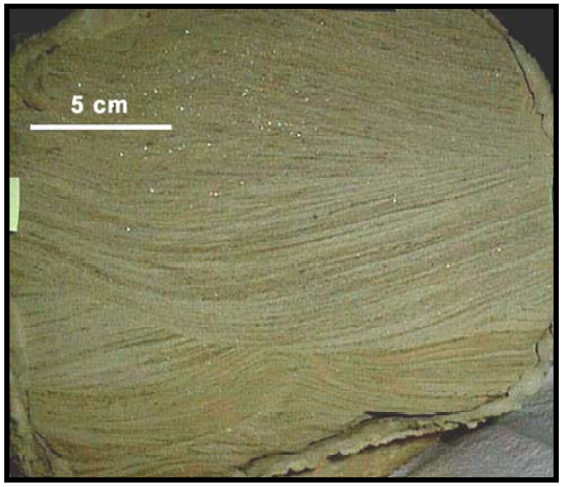


Hanford formation



Cold Creek Unit





Ringold Formation

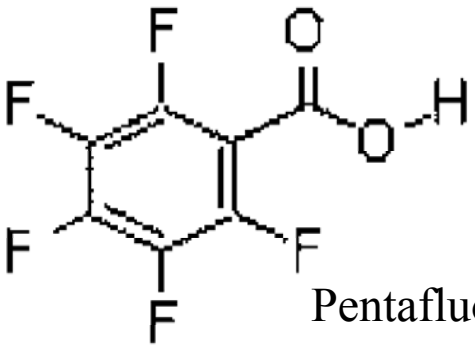
Quantifying hydrologic transport

Decreasing size ⇒ Increasing rate of diffusion

PIPES
D_e = 5.2 x 10^{-10} m^2 s^{-1}
pK_a = <3, 6.8

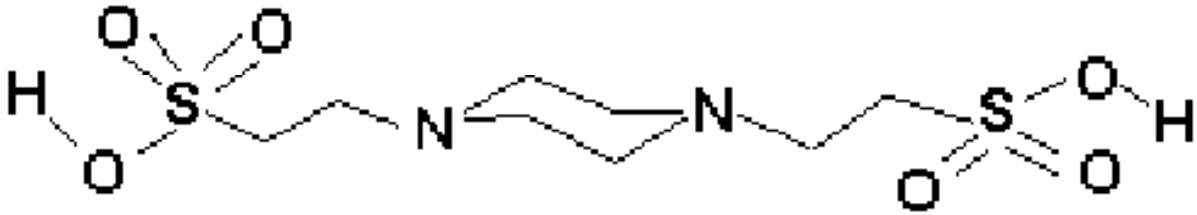
PFBA
D_e = 7.8 x 10^{-10} m^2 s^{-1}
pK_a = 2.7

Br^-
D_e = 18.7 x 10^{-10} m^2 s^{-1}

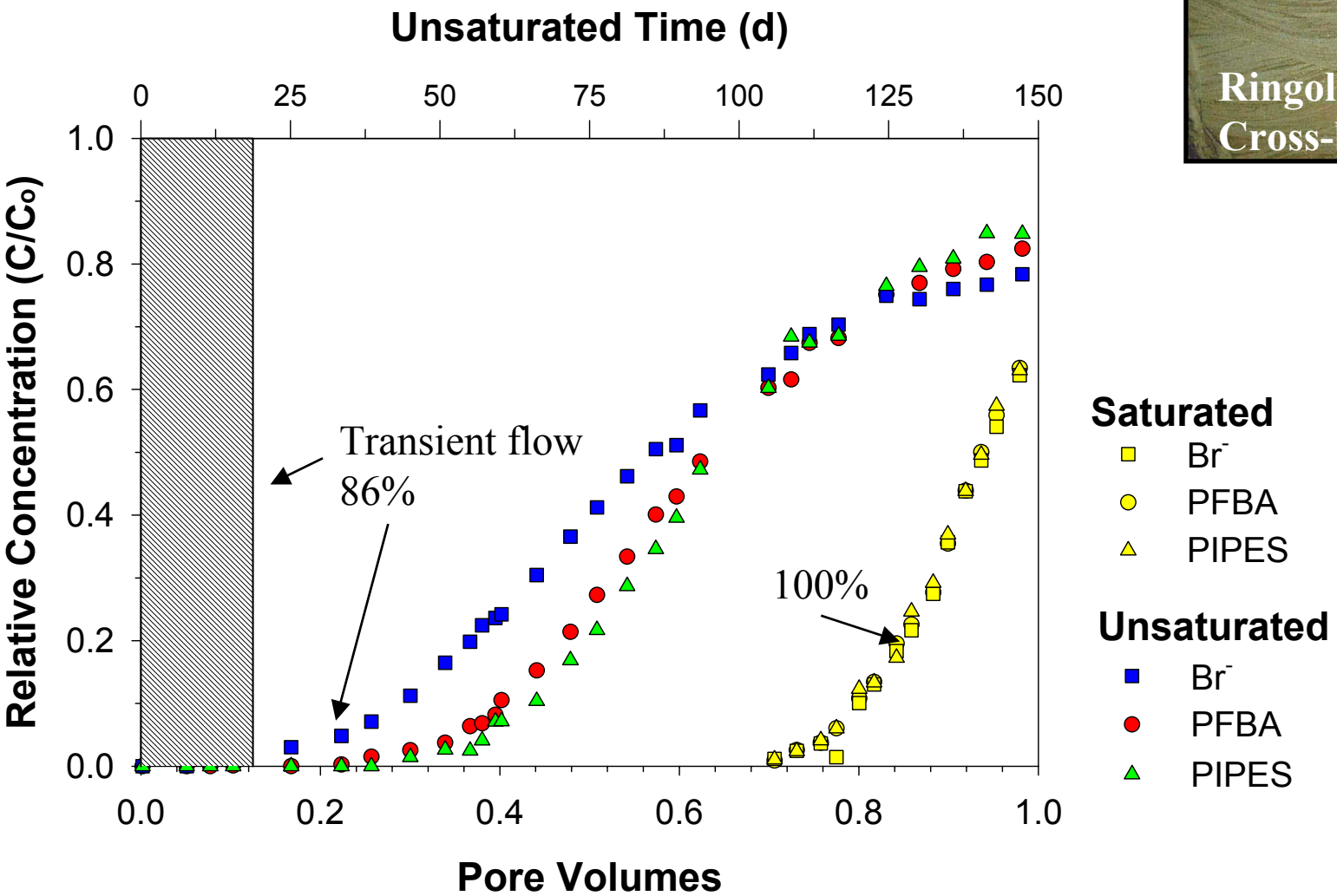


Pentafluorobenzoic acid

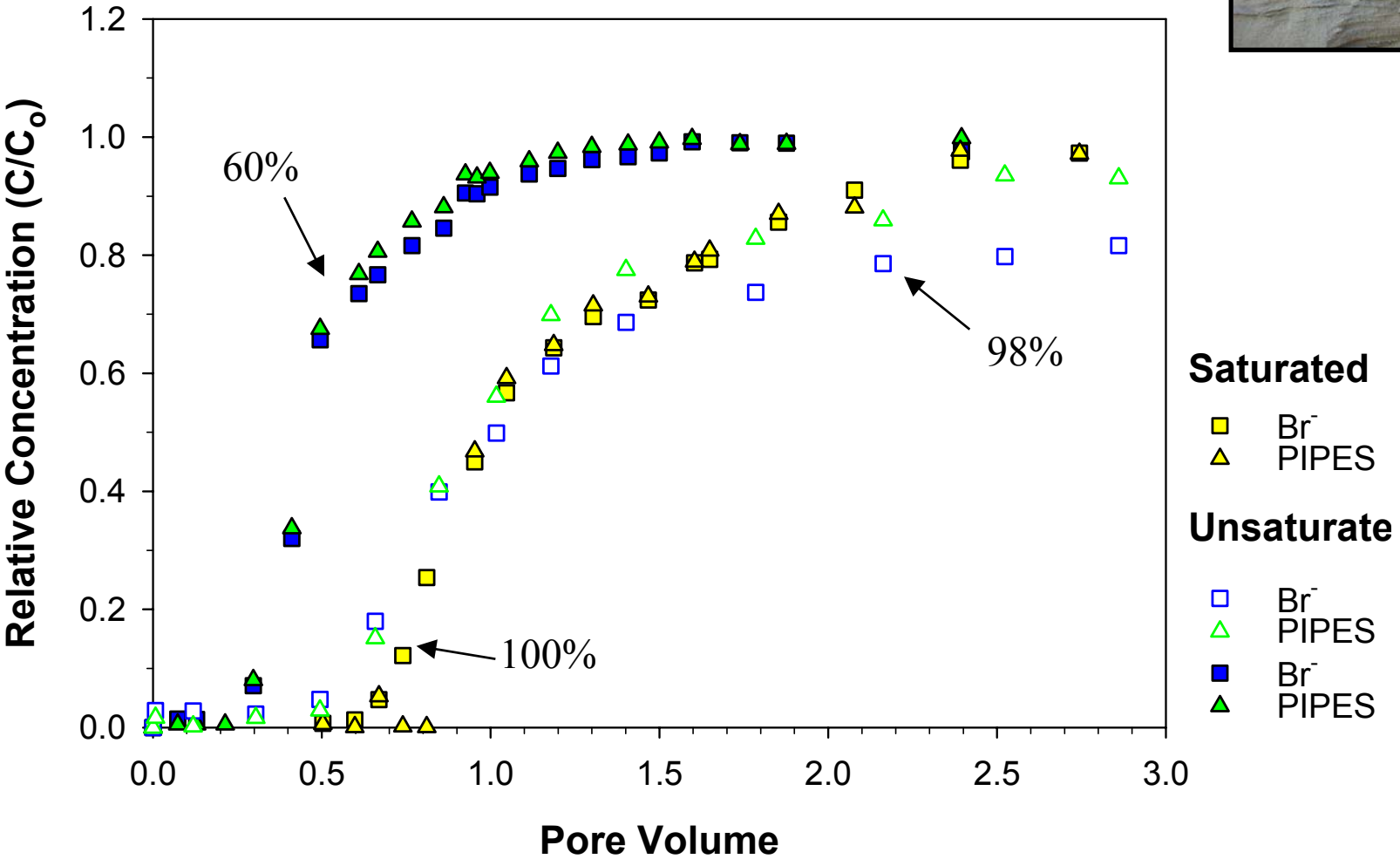
1,4 Piperazinebis (ethanesulfonic acid)



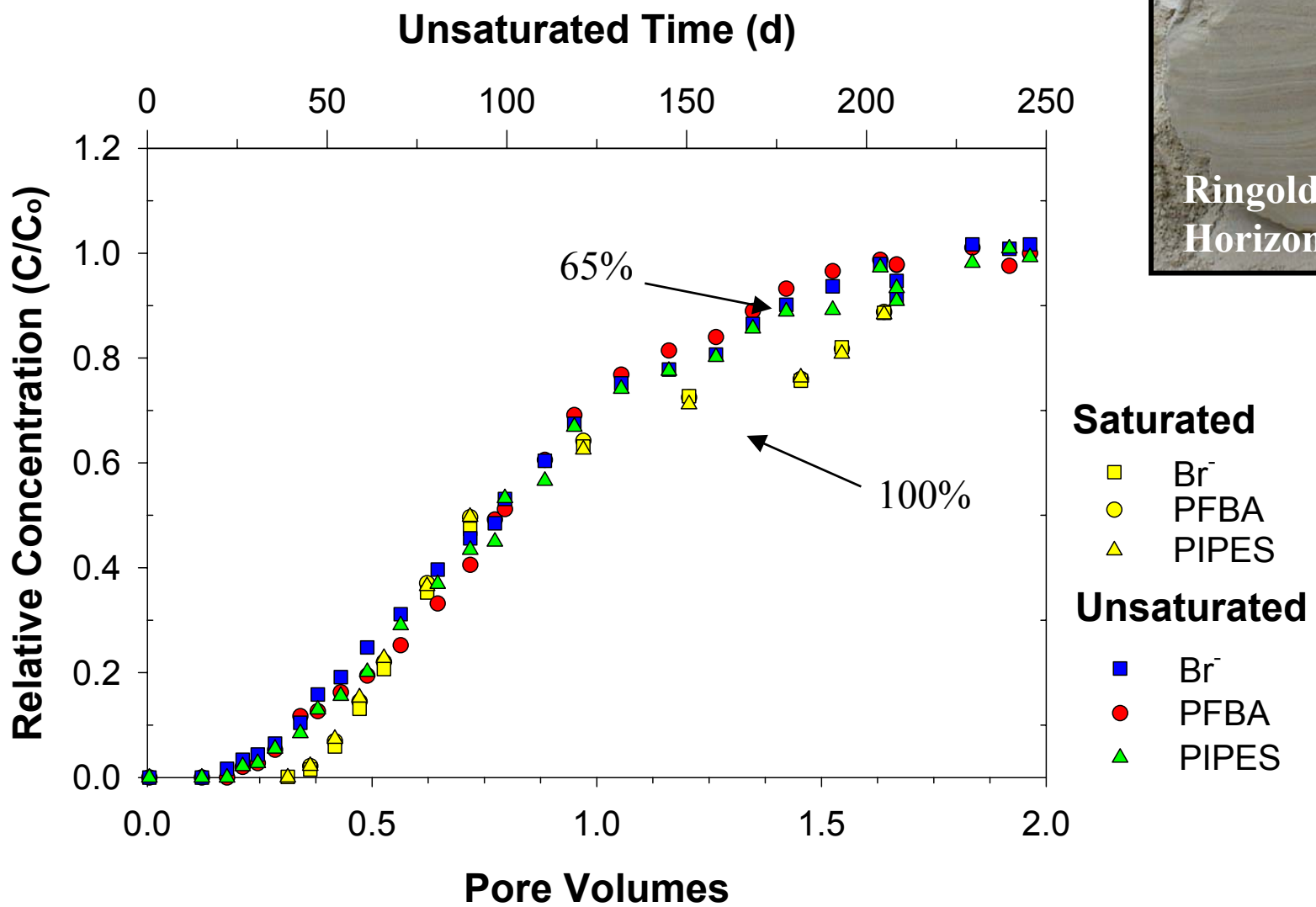
Finger flow and perched immobile water during unsaturated flow in cross-bedded laminated media



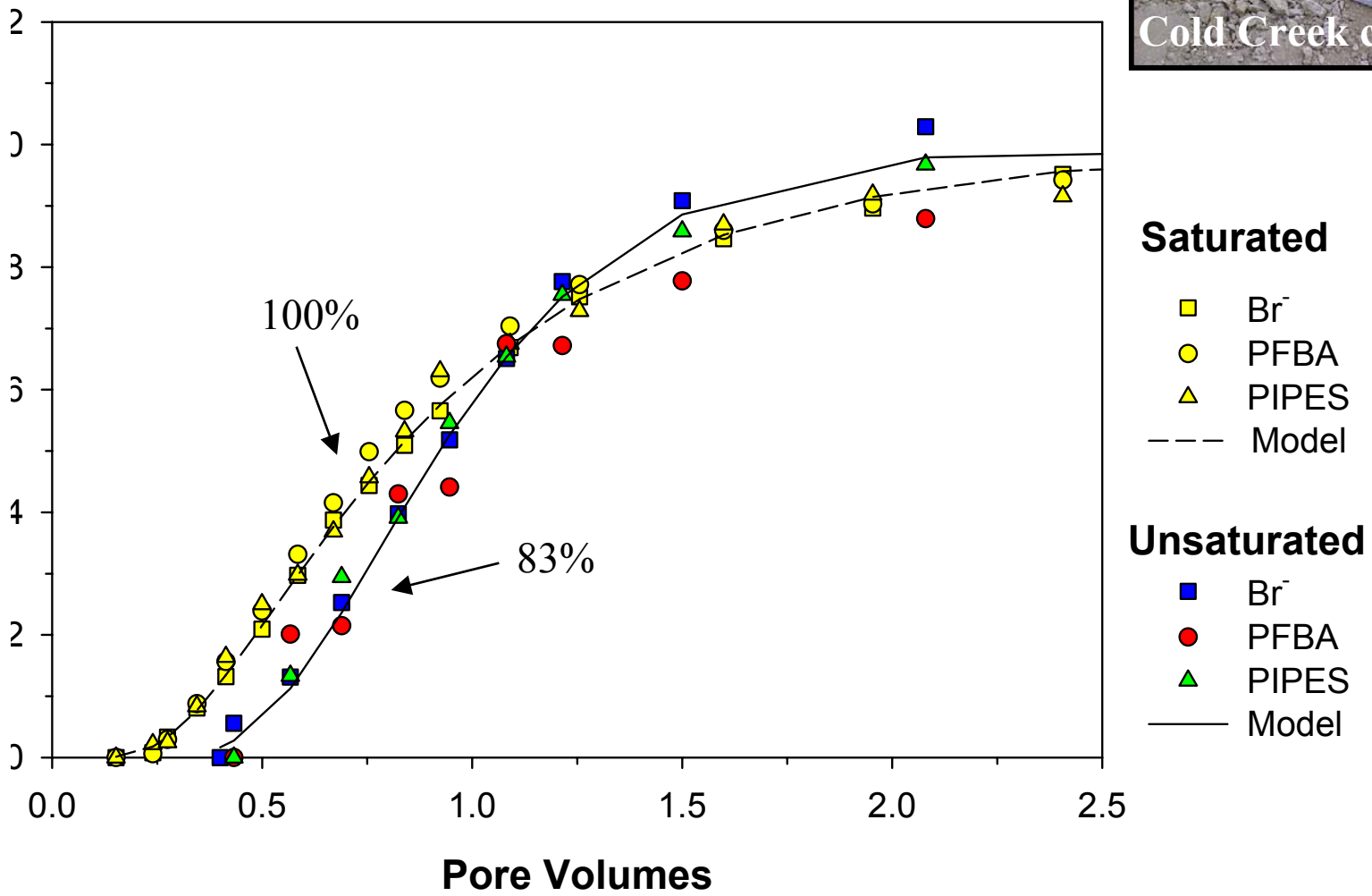
Finger flow and limited formation of immobile water in laminated and rippled Hanford fines



Tracer diffusion is inhibited by the formation of capillary barriers in horizontally-bedded laminated media

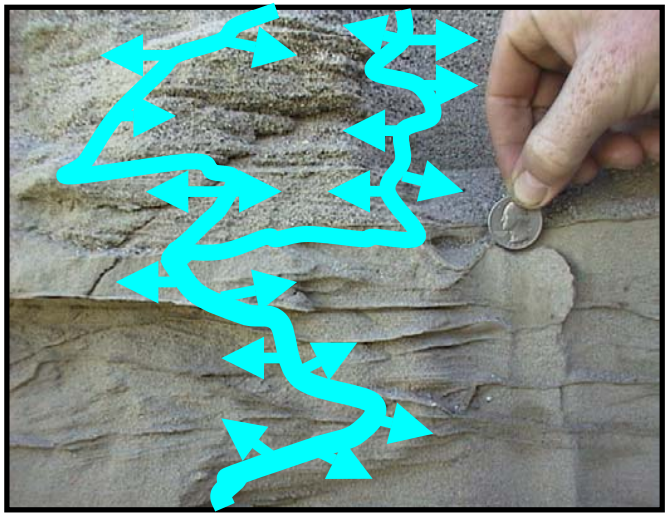


Minimal preferential flow, minimal development of immobile water due to secondary fillings of pores with calcite

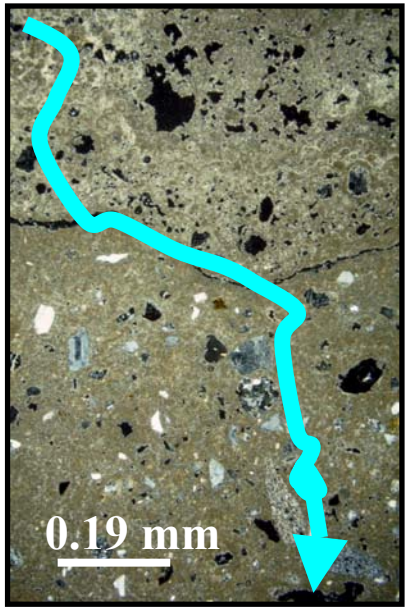


Conceptual hydrologic models

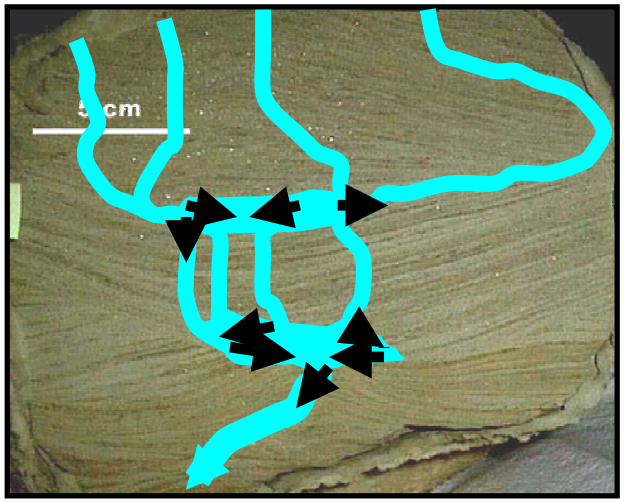
HANFORD
LAMINATED FINES

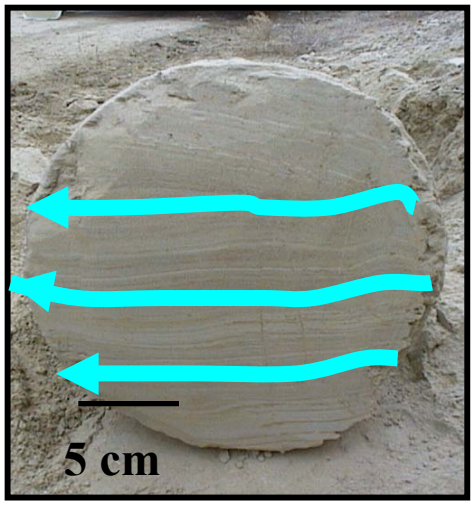


CALICHE

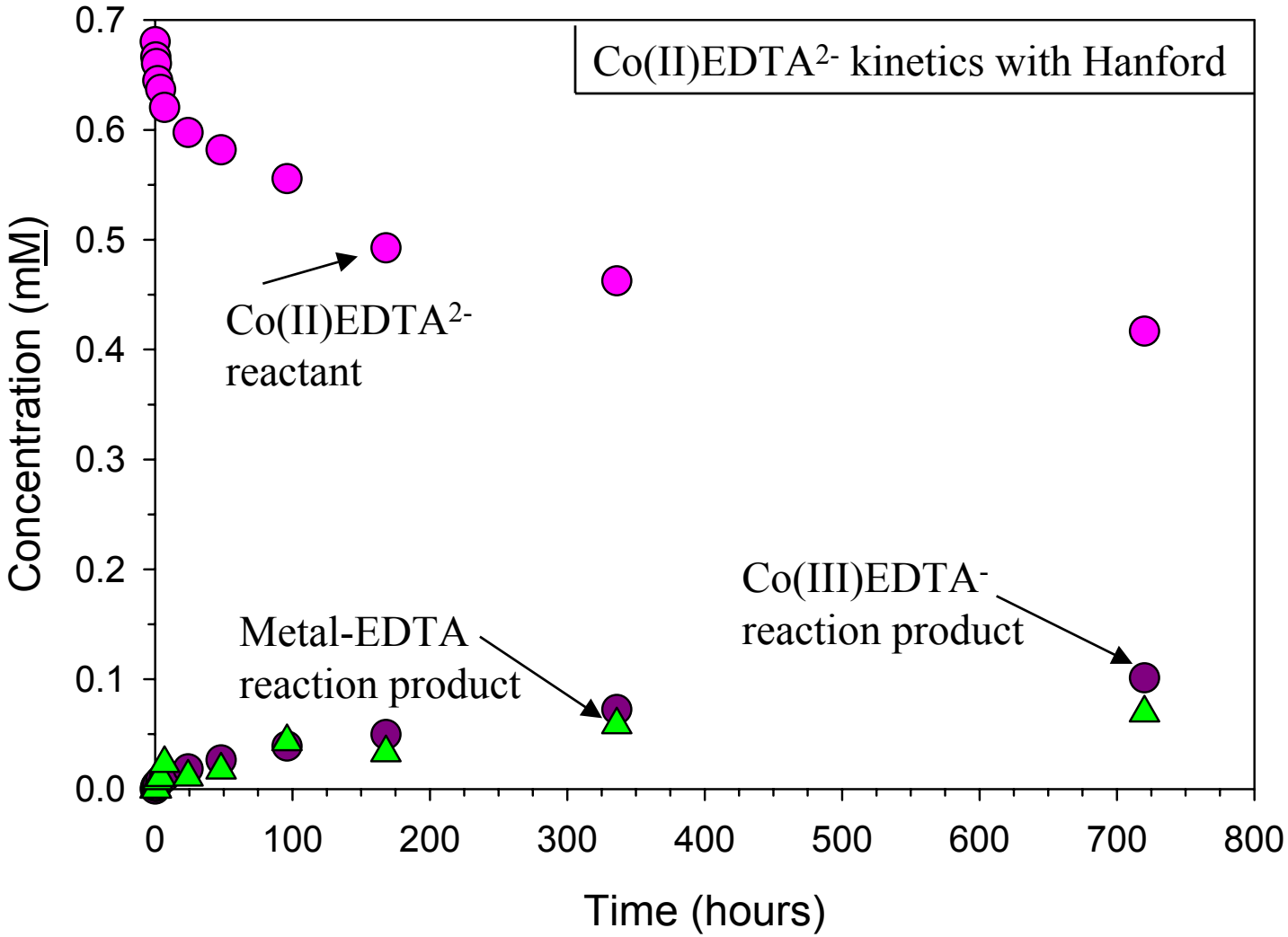


RINGOLD
LAMINATED FINES

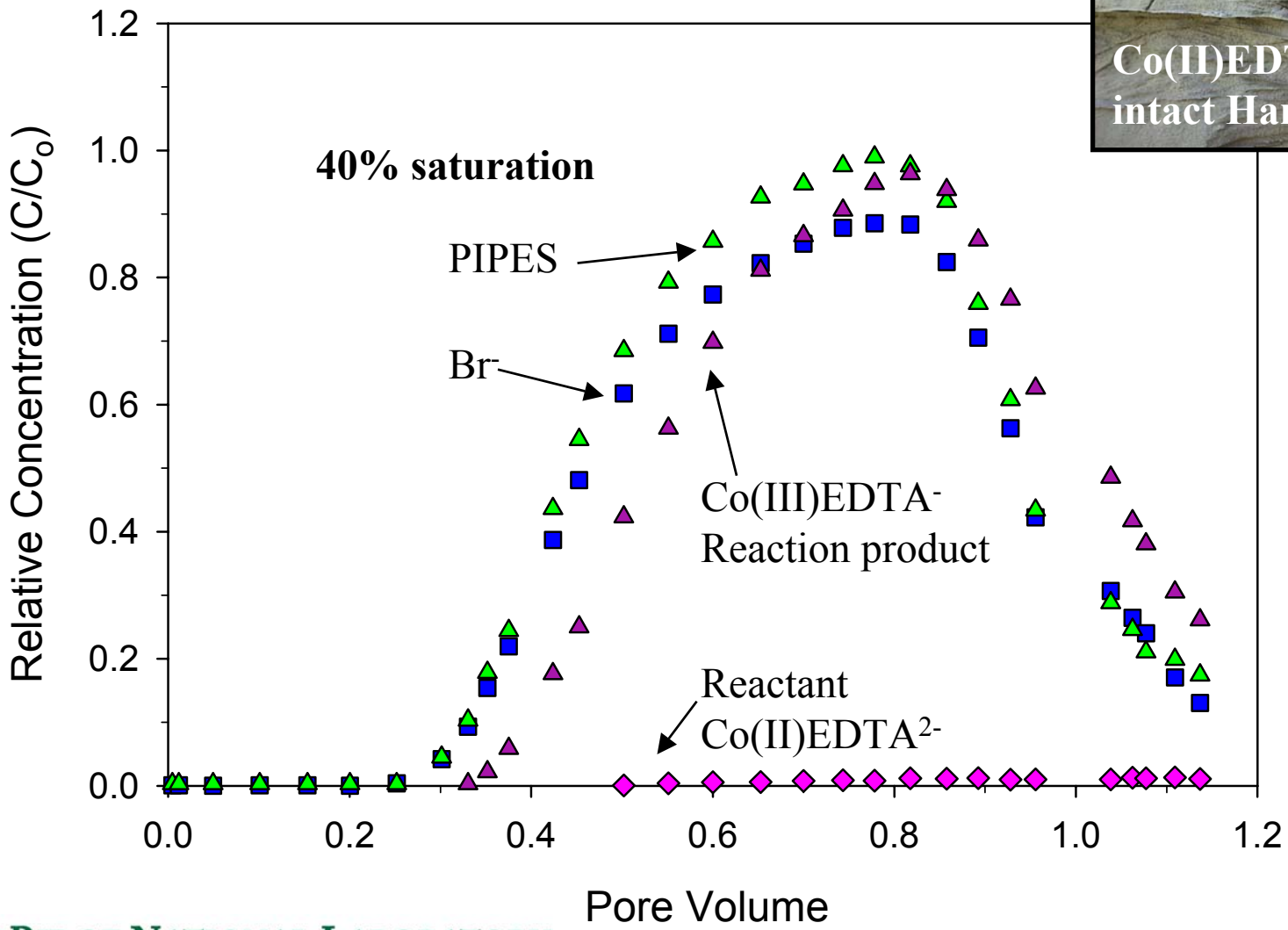




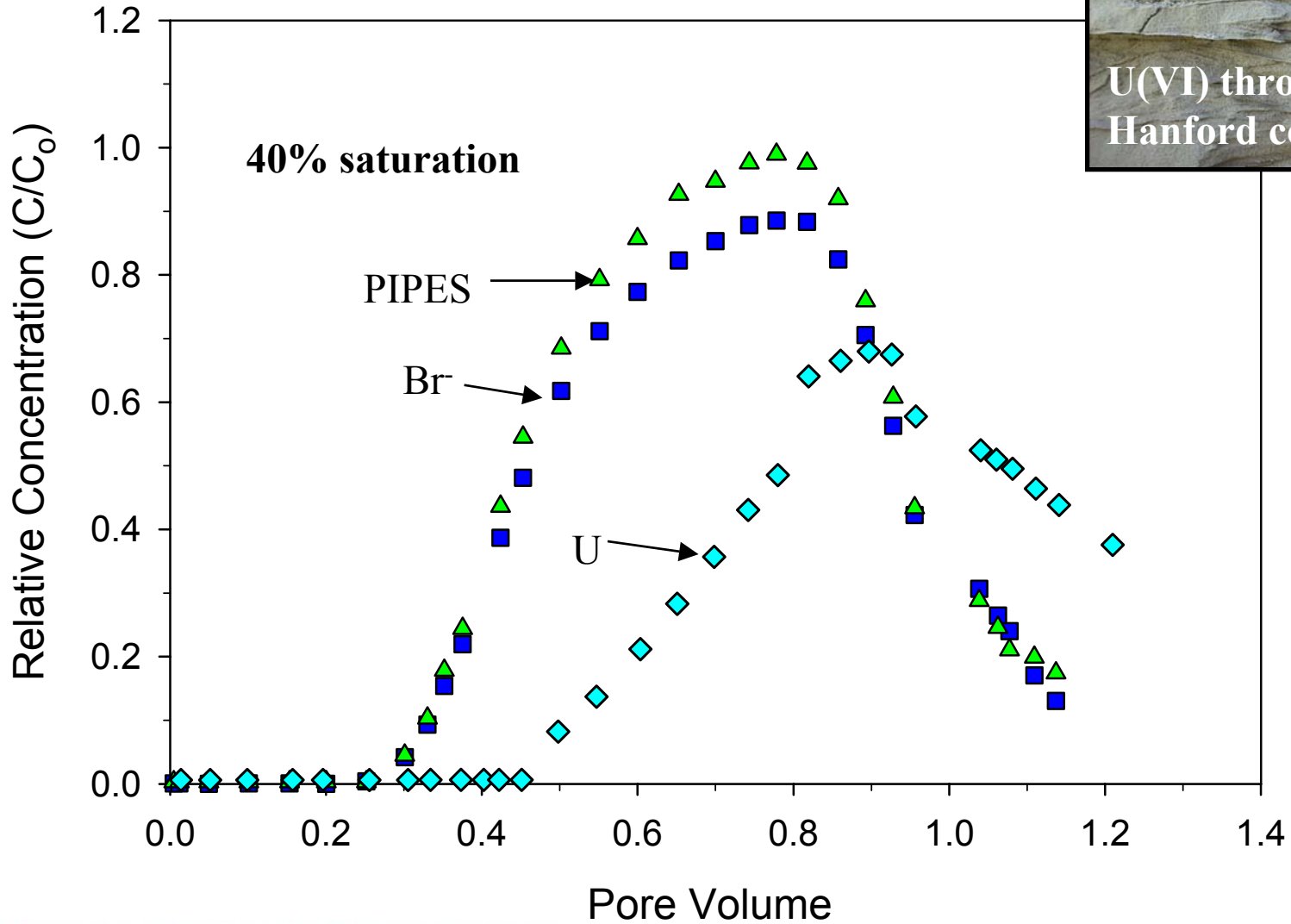
Oxidation of $Co(II)EDTA^{2-}$ to $Co(III)EDTA^{-}$ by Hanford sediments



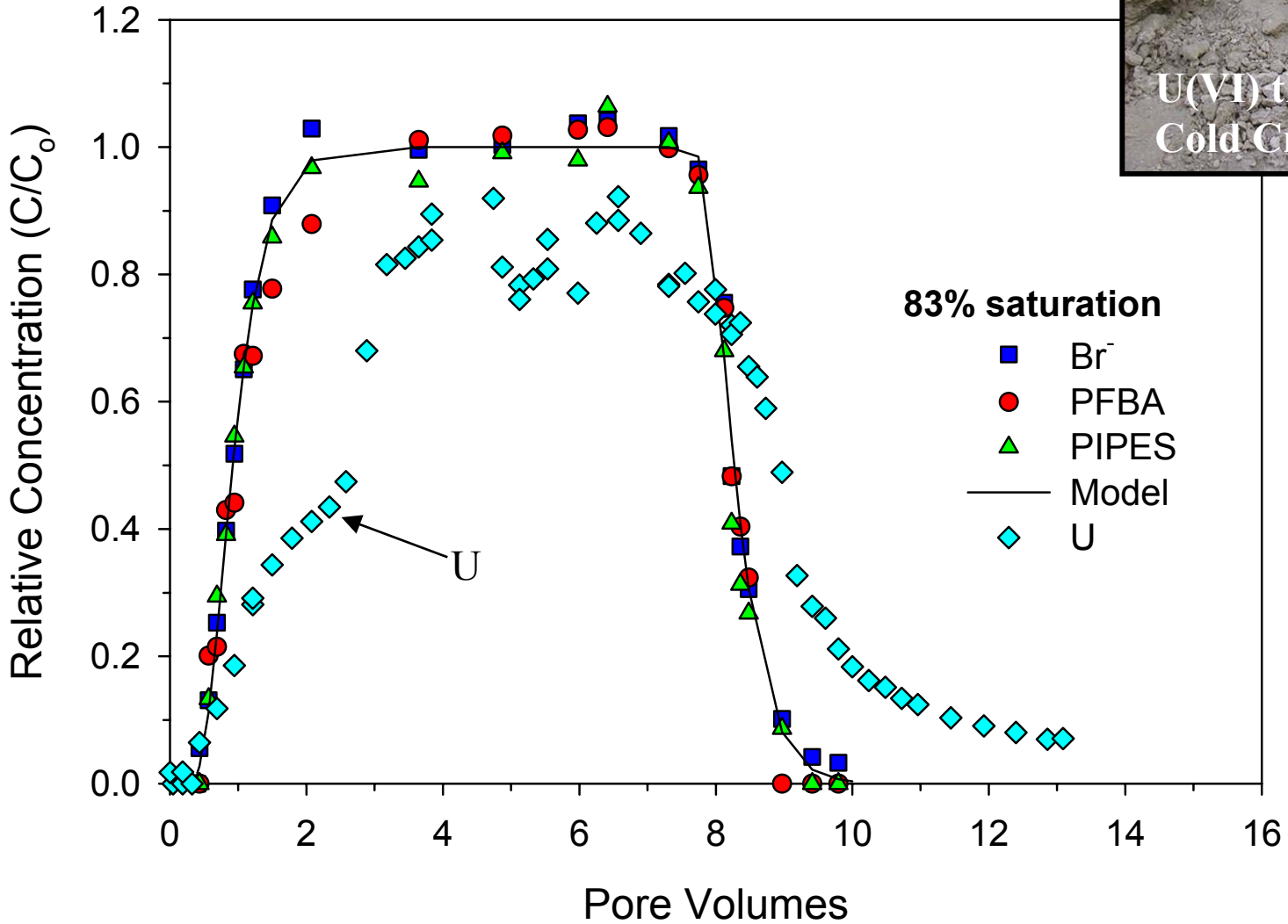
Oxidation reaction is robust despite finger flow and media bypass in unsaturated Hanford core



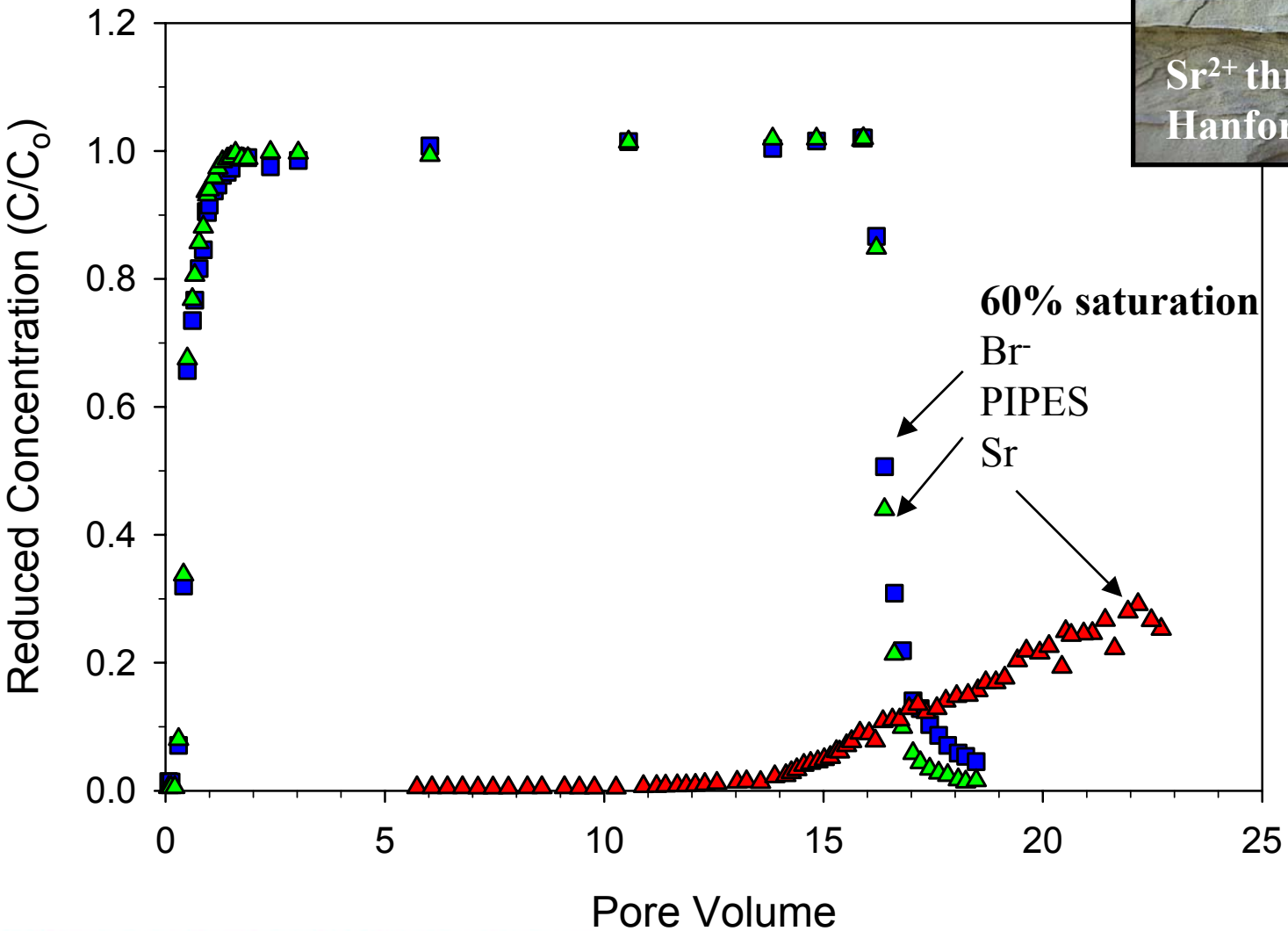
Significant retardation of U despite finger flow and media bypass in unsaturated Hanford core



Significant retardation of U, minimal preferential flow and immobile water in the caliche



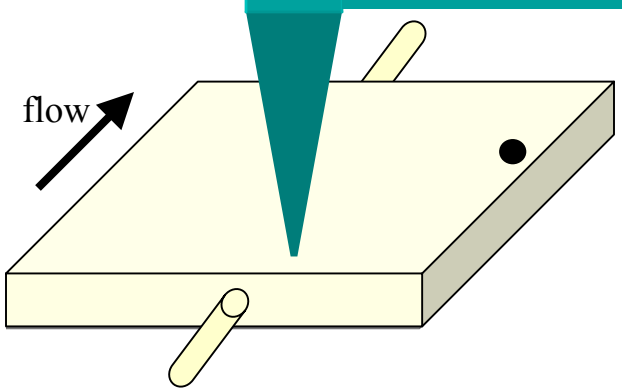
Sr^{2+} is highly reactive with the Hanford formation, despite finger flow and extensive media bypass



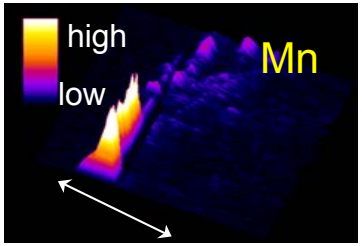
Determining surface-mediated reaction mechanisms

- X-ray adsorption spectroscopy
- Mossbauer spectroscopy
- Micro-Raman spectroscopy

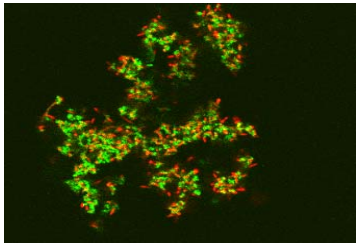
In-situ, Real-time Spectroscopic and Microscopic Characterization



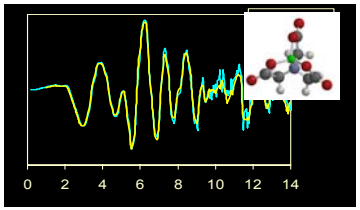
- Identification of surface phases and principal sorbents under dynamic-flow conditions.
- Mineral grains mounted within flow-cell equipped with optically transparent window permitting microscopic and micro-spectroscopic examination



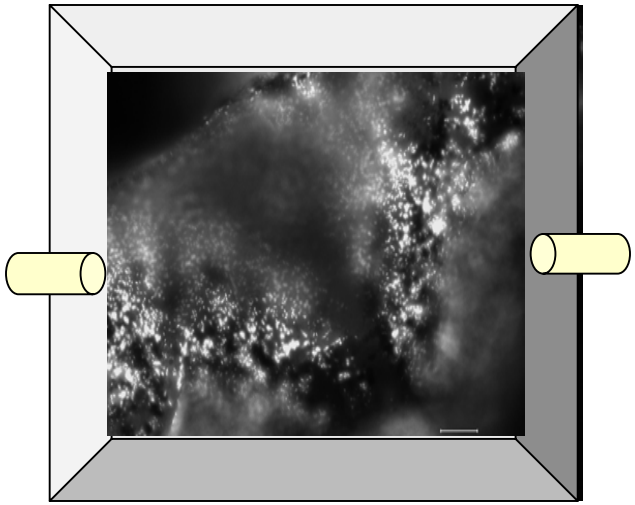
Elemental distribution with x-ray fluorescence imaging



Bacterial distribution using epifluorescence and laser confocal microscopy



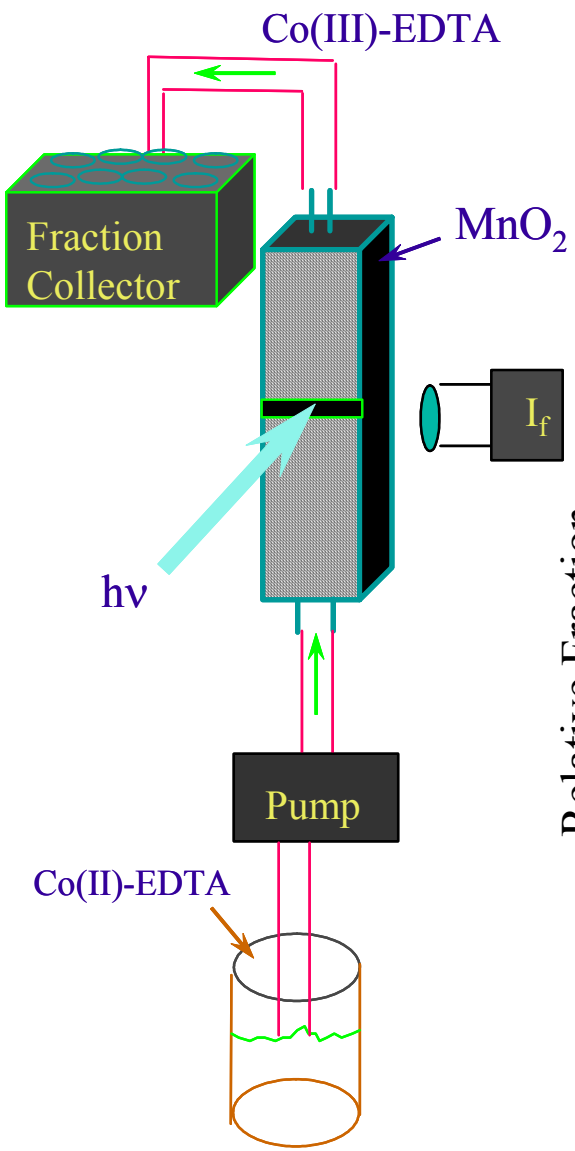
Surface phases and sorbents identified with Raman and X-ray absorption spectroscopies



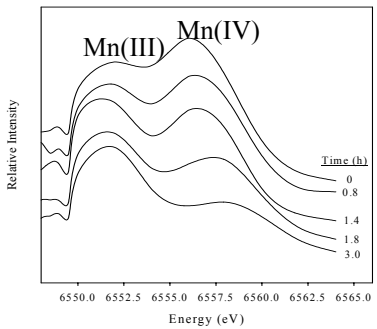
Phase-contrast image of quartz grains with deposits of amorphous iron oxide

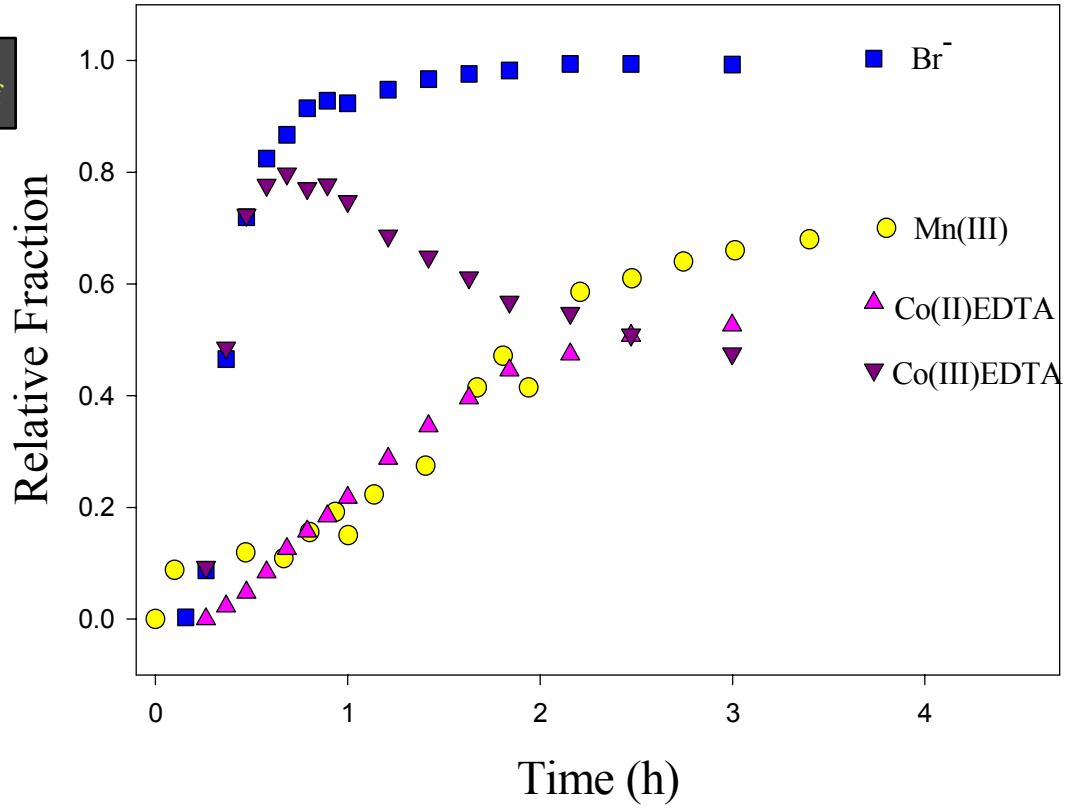
^{60}COBALT MOBILITY

In Situ Speciation of Co and Mn under Hydrodynamic Conditions using XAS



- Co(III)EDTA$^-$ production
- MnO_2 oxidant
- Passivation of MnO_2 from the development of Mn_2O_3 layer





Implications

- Physical hydrology
  - Multiple conceptual models that are dependent upon the arrangement of media pore structure, grain size, and water content.
  - Identification of preferential finger flow, immobile water, local-scale perching, and lateral spreading
  - Isolation of flowpaths to specific mineralogies (e.g., clays, Fe- and Mn-oxides, biotite) in sediments with decreasing water content.
- Coupled hydrology and geochemistry
  - Transport through intact sediments is complex, resulting in "accelerated" ($Co(III)EDTA^-$) or "retarded" transport (U, Sr).
  - Importance of physical and/or geochemical nonequilibrium.

Future Work

- Obtain additional intact cores of Hanford from the ERDF.
- Initiation of Cr(VI) investigation, continuation of U and Co-chelate (EDTA, HEDTA) experiments.
- Continuation of novel surface techniques to determine mechanisms governing chelated metal, U, and Cr(VI) adsorption and transformation.
- Dye-trace and dissembly of intact cores to ground-truth coupled processes.
- Modeling coupled processes in intact cores.
  - Multipermeability hydrologic processes
  - Multicomponent, multiprocess fate and transport