FIELD EXPERIMENTS AND CHARACTERIZATION

FOR

REACTIVE RADIONUCLIDE TRANSPORT

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by

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ADVANCED VADOSE ZONE CHARACTERIZATION WORKSHOP

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MODELING PHILOSOPHIES

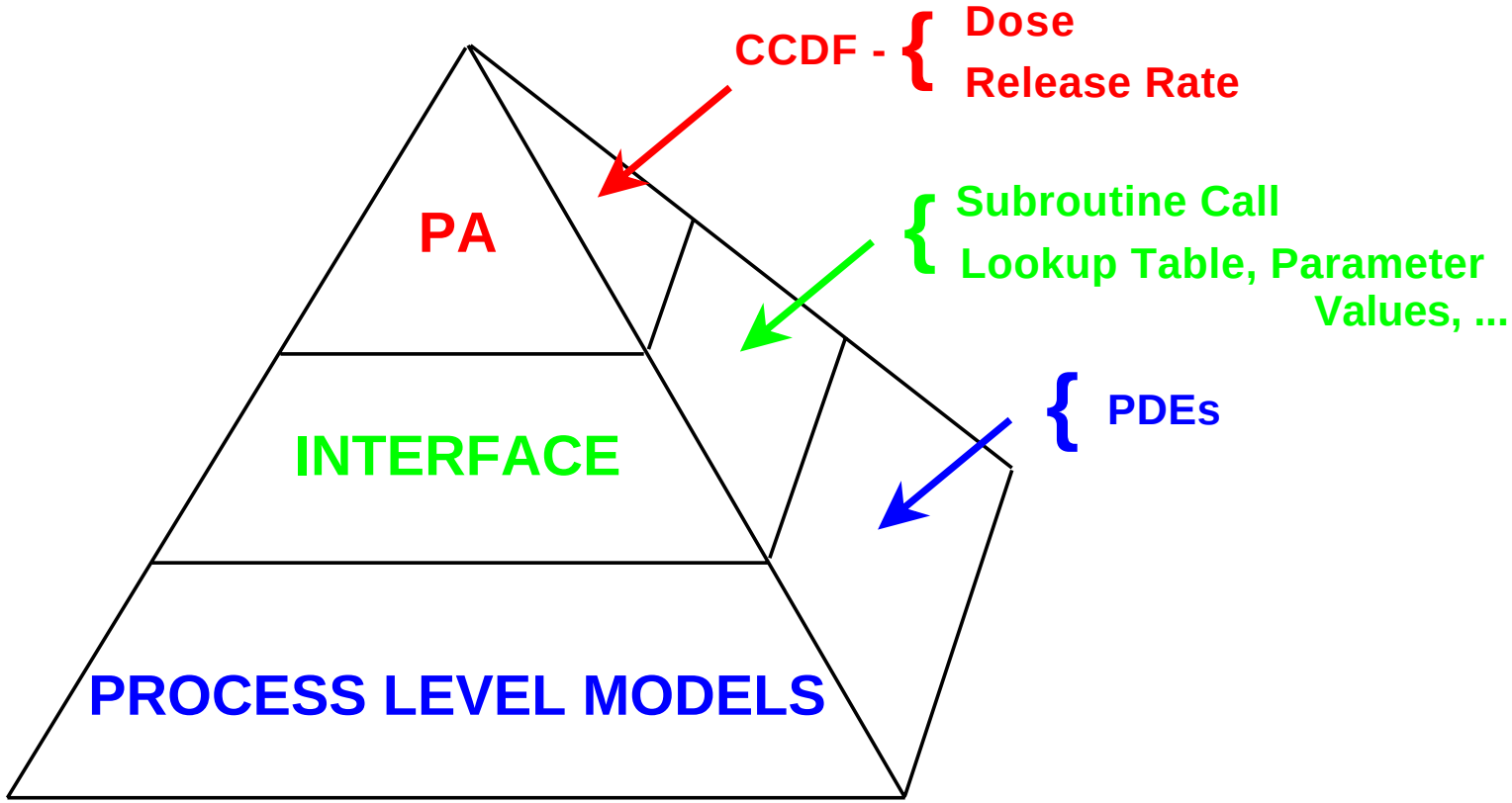
MODEL USAGE: Models serve the purpose to distinguish, constrain and/or confirm possible mechanisms which may be difficult to determine directly from field or experimental data through intuition/common sense/experience.

- **AID PROCESS-LEVEL UNDERSTANDING (Process Level Model-PLM)**
  - **Understand Dominant Mineral Transformations**
  - **Silica Buffering Phases**
  - **pH Neutralizing Reactions**
  - **Radionuclide Transport in Strong Background Electrolyte Solution**

    $$\text{K-Feldspar} + H^+ + H_2O \longrightarrow K^+ + Al(OH)_3 + SiO_2$$

    $$XCs + K^+ \rightleftharpoons XK + Cs^+$$
- **AS PREDICTIVE TOOL**
  - **Use Historical Record to Calibrate Model**
  - **Link PLM to Site Scale Model**
  - **Provide Source Term to Saturated Zone Model**

MODELING HIERARCHY



- PA–type models are applicable to long time scales required for environmental assessment applications
- Process-Level models provide sound foundation for PA models and are necessary for modeling short (engineering) time scales

LAUNDRY LIST OF CHEMICAL DATA NEEDS FOR HANFORD MODELING EFFORT

- **SEDIMENT CHARACTERIZATION**
  - **Primary Mineral Abundances**
  - **Mineral Surface Area (grain size)**
  - **Exchange Capacity/Site Density (bulk or individual mineral)**
  - **Sorption Site Characterization**

- **CHEMICAL SOURCE TERM**
  - **Tank Heat Generation Rate**
  - **Chemical Composition**
  - **Time History of Leak**
  - **Spatial Location(s)**

LAUNDRY LIST OF CHEMICAL DATA NEEDS FOR HANFORD MODELING EFFORT [CONTINUED]

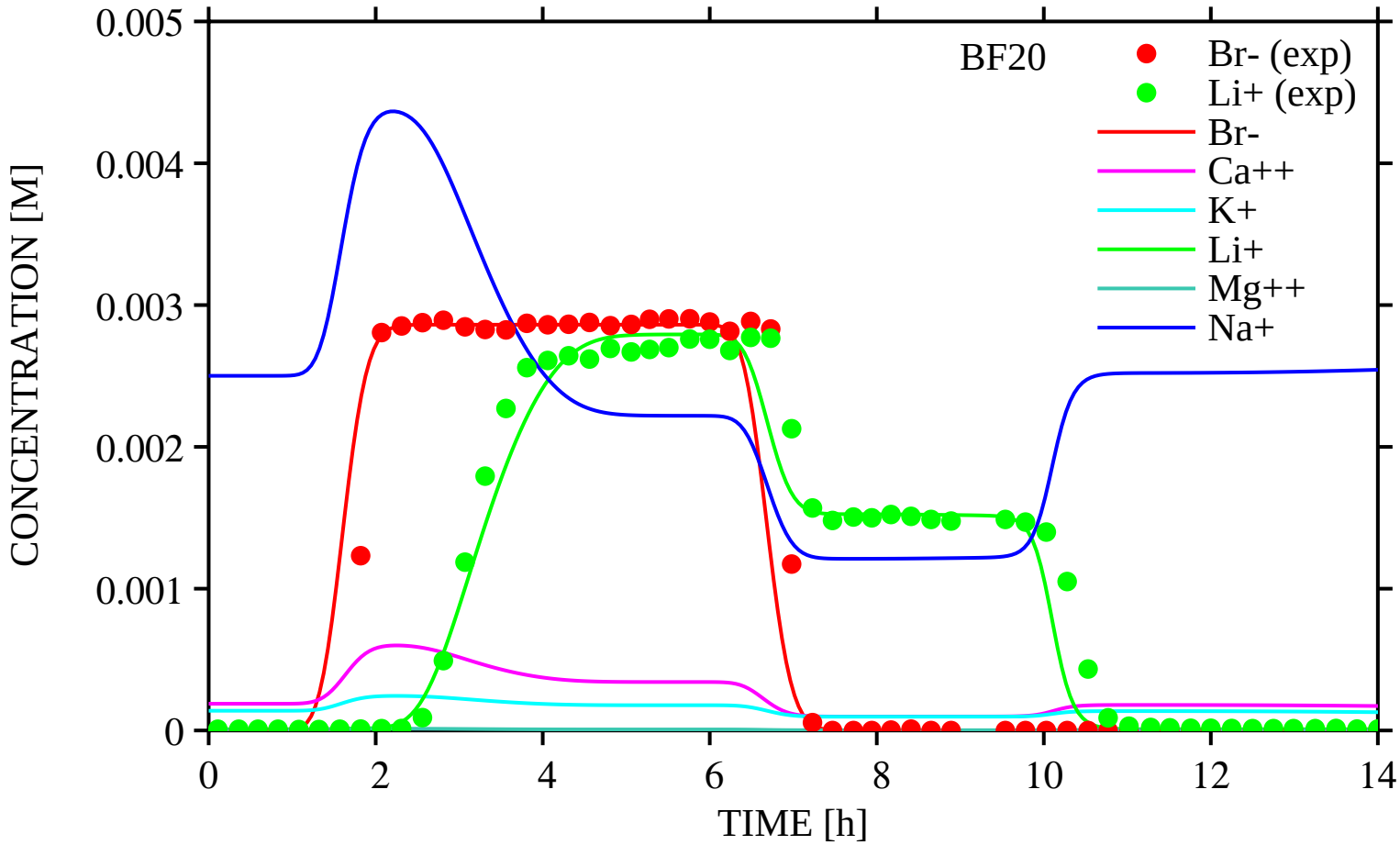
- **THERMODYNAMIC DATA**
  - **Primary and Secondary Minerals, Aqueous Complexes, Solid Solutions . . .**
  - **Sorption Selectivity Coefficients (Ion Exchange, Surface Complexation)**
  - **High Ionic Strength Model Parameters**
- **KINETIC DATA**
  - **Rate Mechanisms (pH-dependence, . . .)**
  - **Rate Constants & Mineral Surface Areas**
  - **Sorption Kinetics**
  - **Nucleation Kinetics**
  - **Redox Processes**
- **POROSITY/PERMEABILITY/TORTUOSITY CONSTITUTIVE RELATIONS RELATED TO CHEMICAL ALTERATION**

RADIONUCLIDE SURROGATES

Radionuclide	Surrogate
NpO_2^-	Li^+
NpO_2^-	Co^{2+}
NpO_2^-	Ni^{2+}
NpO_2^-	Mn^{2+}
Pu^{3+}	Sm^{3+}
PuO_2^+, PuO_2^{2+}	UO_2^{2+}
PuO_2^{2+}	MoO_2^{2+}
Pu^{4+}	Hf^{4+}
Am^{3+}	Ce^{3+}
Am^{3+}	Eu^{3+}
TcO_4^-	SeO_4^-
TcO_4^-	ReO_4^-
TcO_4^-	MoO_4^-

Red indicates tracers that have actually been used in field tests.

C-HOLES COLUMN EXPERIMENT



EXPERIMENT: C-Holes Site, Well C#2, Depth 2406 ft (below surface). Rock Type: Crater Flat Tuff Formation, Bullfrog Tuff Member, Central Flow Zone. Rock crushed and wet sieved to a particle size range of 75-500 microns. Column Dimensions: 91.4 cm long by 0.62 cm diam (Tim Callahan & Paul Reimus).

ION EXCHANGE - MINERAL REACTION INTERACTION

- **COUPLED REACTIONS**

$$\underbrace{X_m^\alpha \mathcal{A}_j + \mathcal{A}_k \rightleftharpoons X_m^\alpha \mathcal{A}_k + \mathcal{A}_j}_{Ion\ Exchange} \quad (fast); \qquad \underbrace{\sum_j \nu_{jm} \mathcal{A}_j \rightleftharpoons \mathcal{M}_m}_{Mineral\ Rxn.} \ (slow)$$

- **MASS TRANSPORT EQUATIONS**

$$\frac{\partial}{\partial t}\left\{\phi \underbrace{\left[S_l \Psi_j^l + S_g \Psi_j^g\right]}_{Aqueous+Gaseous\ Conc.} + \underbrace{\sum \overline{C}_j^{m\alpha}}_{Sorbed\ Conc.}\right\} + \nabla \cdot \left(\underbrace{\Omega_j^l + \Omega_j^g}_{Flux} + \underbrace{q_c \sum \overline{C}_j^{\mathrm{coll}}}_{Colloid\ Flux}\right)$$

$$= \underbrace{-\sum_m \nu_{jm} I_m}_{Mineral\ Rate\ Term}$$

$$\frac{\partial \phi_m}{\partial t} = \overline{V}_m I_m \qquad (Mineral\ Mass\ Transfer\ Eqn.)$$

- **EXCHANGE SITE DENSITY**

$$\omega_m^\alpha = \underbrace{Q_m^\alpha}_{CEC} \underbrace{\rho_m \phi_m}_{Mineral\ Conc.}$$

DISTRIBUTION COEFFICIENT: K^D

- **DEFINITION**

$$\widetilde{K}_j^D = \frac{\overline{N}_j}{N_j} = \frac{\overline{N}_j/M}{N_j/V_{pore}}\frac{M}{V_{pore}} = \frac{\sum \overline{C}_j^{m\alpha}}{\phi\Psi_j}$$

$$= \frac{\rho_{bulk}}{\phi}K_j^D$$

- **RETARDATION FACTOR**

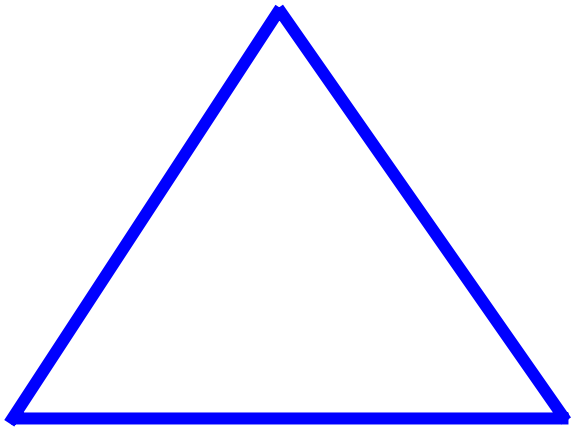
$$R_j = 1 + \widetilde{K}_j^D = 1 + \frac{\rho_{bulk}}{\phi}K_j^D$$

$$\frac{\partial}{\partial t}\left\{\phi R_j \Psi_j\right\} + \nabla\cdot\Omega_j = -\sum_m \nu_{jm} I_m$$

$$\frac{\partial}{\partial t}\left(\phi\Psi_j\right) + \nabla\cdot\left(\frac{\Omega_j}{R_j}\right) = -\frac{1}{R_j}\sum_m \nu_{jm} I_m - \left(\phi\Psi_j\frac{\partial \ln R_j}{\partial t} + \frac{1}{R_j^2}\Omega_j\cdot\nabla R_j\right)$$

CHALLENGE

HETEROGENEITY

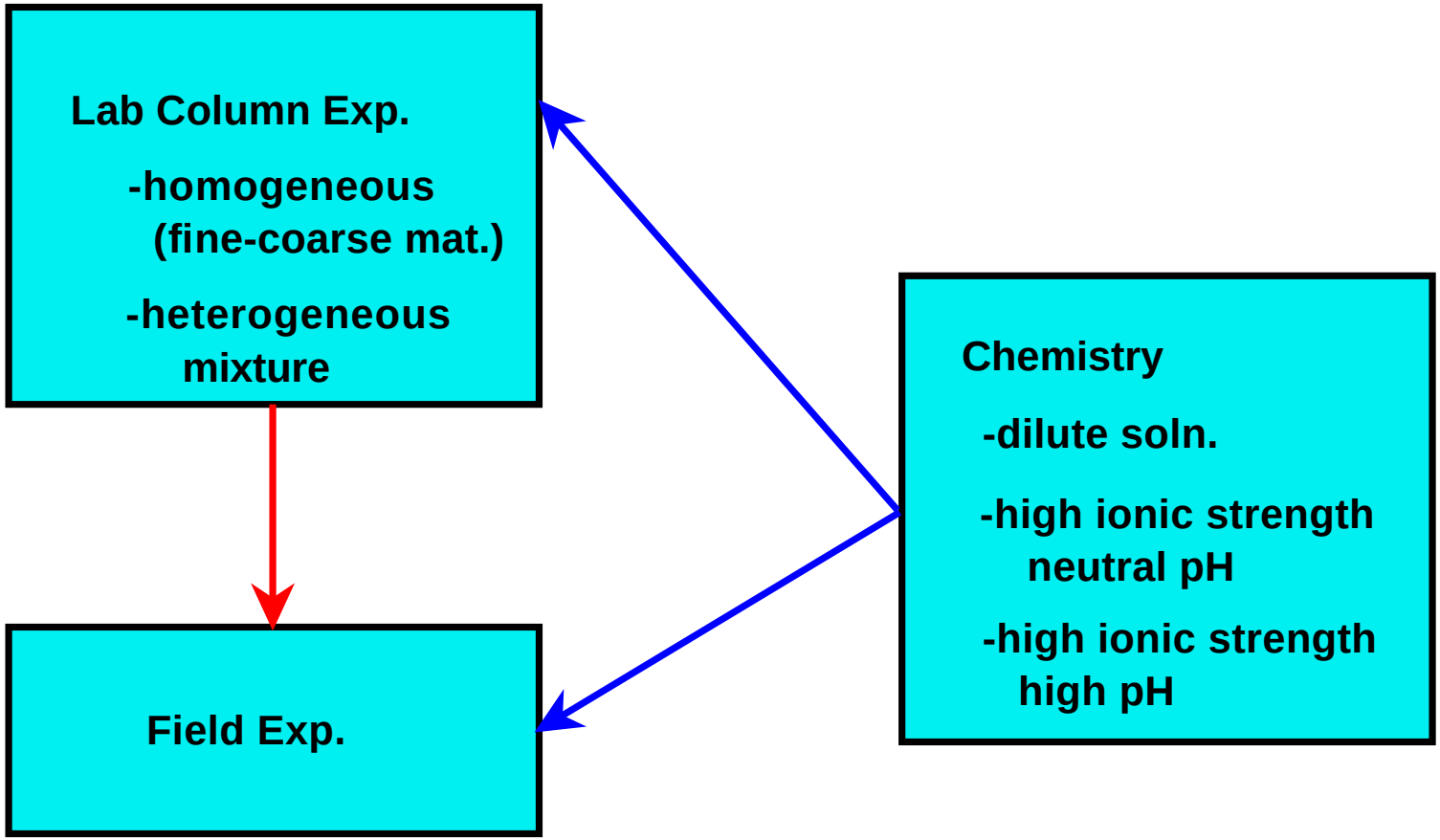


MINERAL REACTION
High pH - High Temp.

COMPETITIVE SORPTION
High Ionic Strength

- **Design experiments to distinguish between sediment heterogeneity, mineral alteration, and competitive sorption.**

FIELD AND LABORATORY EXPERIMENTAL DESIGN



- Combine laboratory column experiments and field experiments in systematic manner to gain maximum information with limited resources.

POSSIBLE REACTIVE TRANSPORT FIELD EXPERIMENTS

- **PURPOSE TO UNDERSTAND BASIC MECHANISMS OF RADIONUCLIDE MOBILIZATION IN THE VADOSE ZONE**
- **HIGH IONIC STRENGTH-HIGH pH SOLUTION**
- **COCKTAIL OF REACTIVE SPECIES**
  - **Surrogate Radionuclides**
  - **Weakly Sorbed Species (Li^+)**
  - **Strongly Sorbed Species (Cs^+, Sr^+)**
- **COLLOIDS**
- **ANALYSIS**
  - **Break-Through Curves**
  - **Mine Back**
- **DIFFERENCES TO ACTUAL SITE**
  - **Surrogates are Different from Radionuclides**
  - **Actual Site Nonisothermal**

POSSIBLE EXPERIMENTAL RESULTS

- ► **UNDERSTAND MECHANISMS FOR EXTENT OF RADIONUCLIDE MOBILITY**
- ► **QUANTIFY HYDROLOGICALLY ACCESSIBLE MINERAL SURFACE AREAS & SORPTION SITES**
- ► **EVALUATE STOCHASTIC VARIABILITY OF SUBSURFACE**
  - **Determine Spatial Correlation Between Hydraulic Conductivity and Reactive Mineral Sites**
- ► **IDENTIFY TIME SCALES OF RELEVANT PROCESSES**
- ► **IDENTIFY PREFERENTIAL PATHWAYS IF THEY EXIST**