Hanford 300 A IFC

Multi-scale Mass Transfer as the Key Science Issue at the Hanford IFC

Definition of Mass Transfer

► Kinetic mass exchange between mobile and immobile domains in subsurface sediments.

- ➤ Biogeochemical reactions: dissolution/precipitation and sorption/desorption reactions;

- ➤ Diffusion in intra-aggregate and intragrain domains, grain fractures, side pores, and microporous grain coatings;

- ➤ Diffusion or slow advection in low permeability zones: clay or silty clay lens and layers.

- ➤ The coupling of above processes

Multi-scale Mass Transfer

Heterogeneity of Porous Media


Grain-scale Mass Transfer
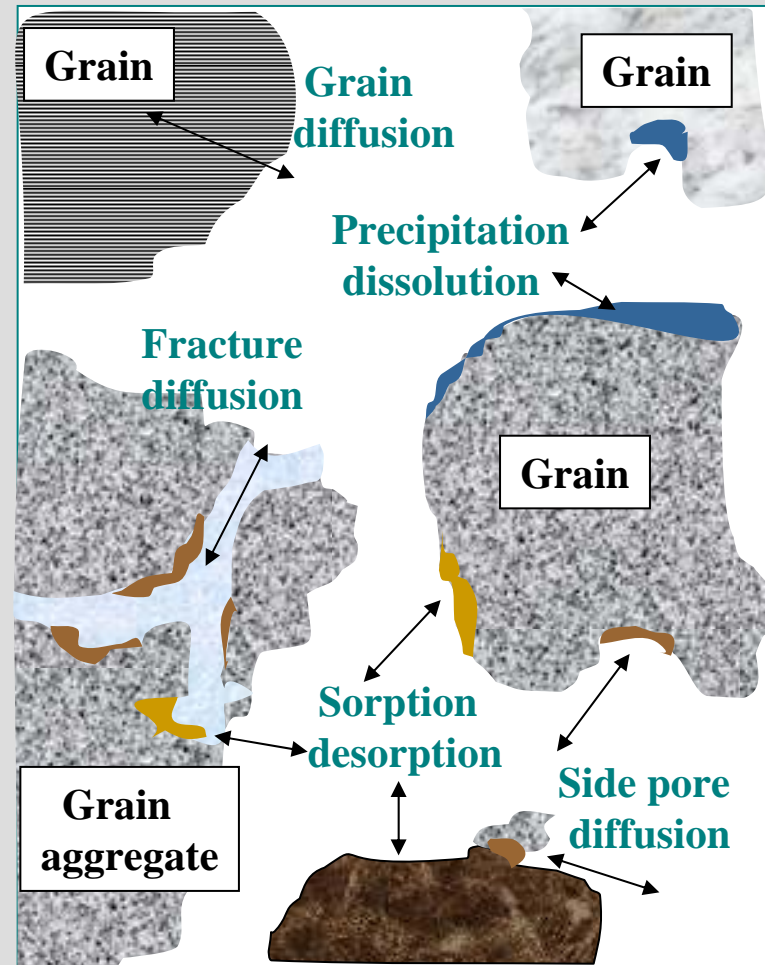
Significance of Mass Transfer

➢ Enhances plume spreading and causes chemical disequilibrium.

➢ Slows effective contaminant desorption and dissolution rates.

➢ Limits the bioavailability or chemical reactivity of sorbed constituents.

➢ Increases times needed for remediation.

➢ Resupplies contaminants to subsurface waters that have been "cleaned".

➢ Complicates remediation strategies based on contaminant desorption, reaction, and immobilization.

Mass Transfer in Homogeneous Systems

Column experiments were performed to investigate mass transfer in homogenized unsieved sediment and its < 2 mm fraction.

Small Column (< 2 mm grains)
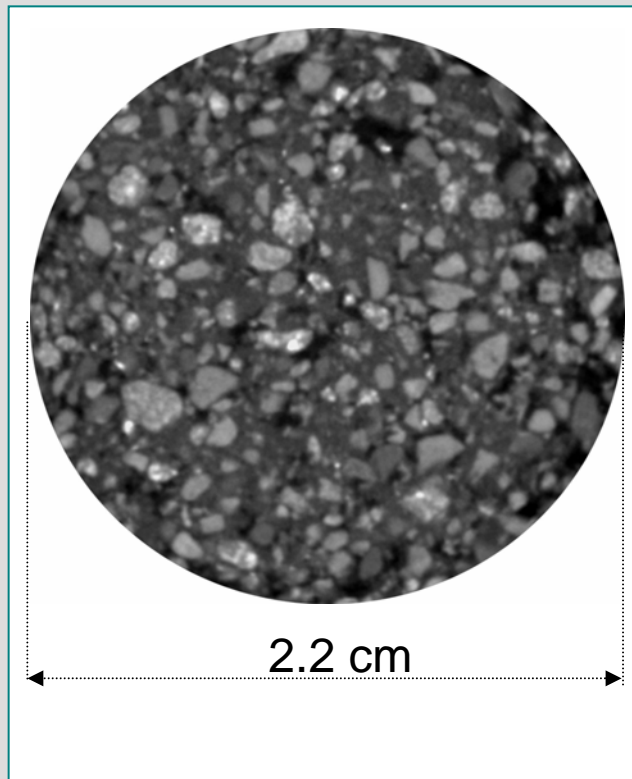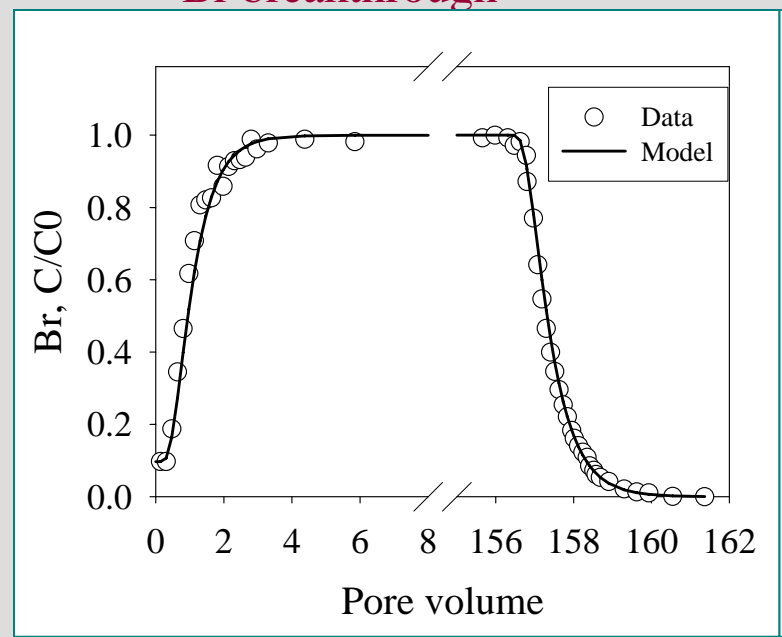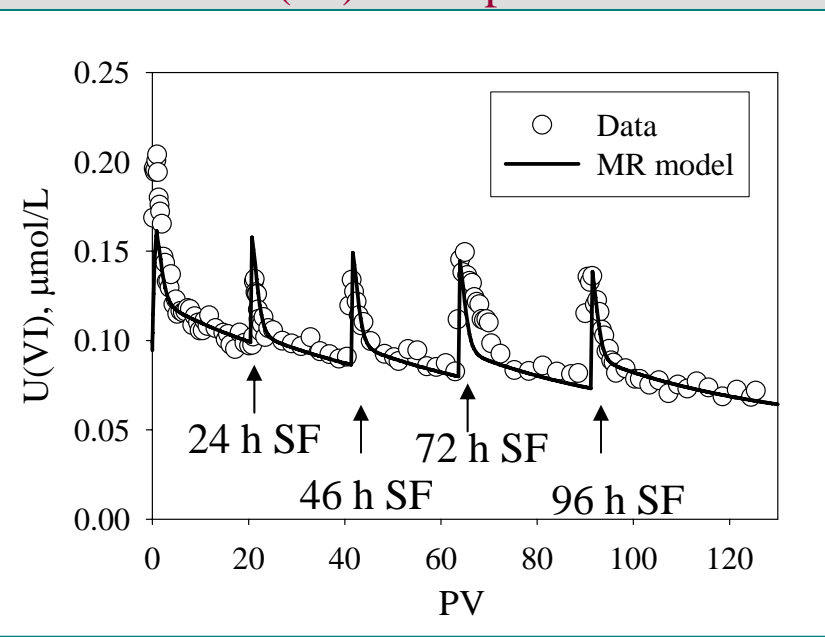
Large Column (80 kg unsieved materials)

2.2 cm

1 cm

Sediment Size and U(VI) Distribution

	Size Range (mm)	Mass Fraction (%)	Total U(VI) (nmol/g)
Cobbles			
	>12.5	74.5	<22
	2.0 – 12.5	17.2	<19
Sand			
	1.0 – 2.0	2.64	26
	0.5 – 1.0	2.34	<18
	0.25 – 0.5	0.78	<21
	0.149 – 0.25	0.33	37
	0.106 – 0.149	0.19	<23
	0.053 – 0.149	0.20	<23
Silt+Clay			
	<0.053	1.78	125
Sand+Silt+Clay	<2.0	8.30	47.81

Mass Transfer in Small Columns (<2mm)
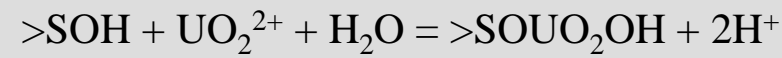
Br breakthrough
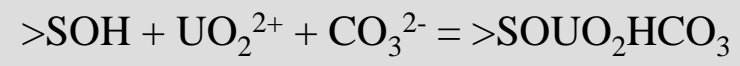
U(VI) Desorption

Multi-rate Model:
$$\frac{\partial q_i}{\partial t} = \int_0^\infty f(\alpha)\alpha(Q_i - q_i)d\alpha$$

q_i: sorbed component i, Q_i: equilibrium sorbed component i, α: rate constant, $f(\alpha)$: rate probability distribution.

Surface Complexation Reactions   log K

$>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^+$ -4.72
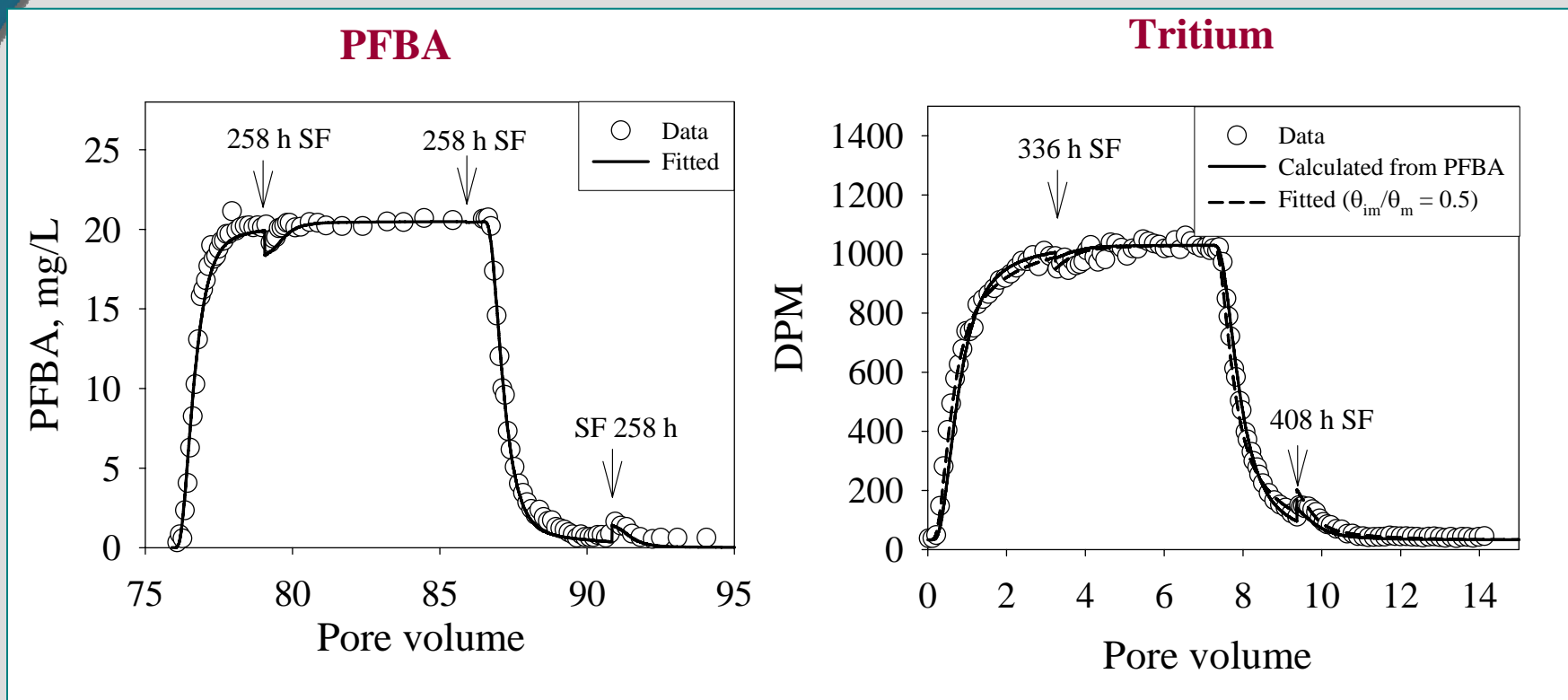
$>SOH + UO_2^{2+} + CO_3^{2-} = >SOUO_2HCO_3$ 16.79
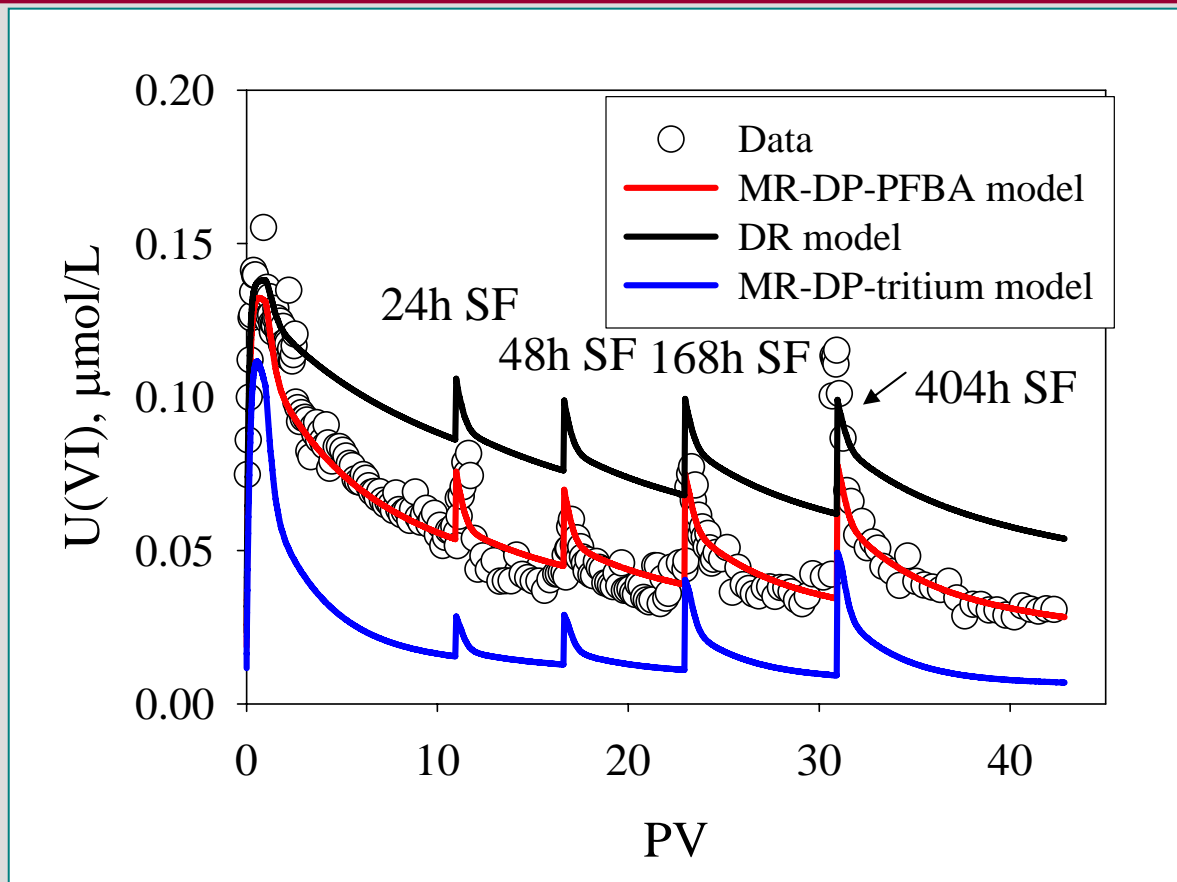
Dual-Domain Mass Transfer in Large Column (Unsieved)

- ➤ Tracer breakthrough curves revealed dual domain mass transfer properties;
- ➤ Mass transfer is species (tracer)-dependent.

U(VI) Mass Transfer in Large Column (Unsieved)

➤ Multi-scale mass transfer processes superimposed with increasing scale.
➤ Importance of selection of tracers in exploring physical mass transfer properties.

Summary

▶ Mass transfer is scale-dependent. Mass transfer processes at different scales will superimpose as the scale increases;

▶ Uranium reactive transport in 300A will be controlled by multi-scale mass transfer processes;

▶ Characterization, scaling, and integration of multi-scale mass transfer processes are challenging, but necessary to understand and project U(VI) reactive transport at the field scale.

Summary (continued)

▶ The development of an effective remediation scheme for the 300A U plume will require explicit consideration of mass transfer

- U(VI) desorption rate and inter-facies mass transfer

- mass transfer of contaminant U(VI) and injected PO_4^{3-} to conincident flow regions for reaction

- long-term reactivity of P.

Upscaling of Mass Transfer Kinetics

Transport Equation:

$$\theta_m \frac{\partial C_i^m}{\partial t} + (1 - \theta_m)\rho_s \frac{\partial q_i^m}{\partial t} = \theta_m AD(C_i^m) - \theta_{im}\beta(C_i^m - C_i^{im}) \qquad i = 1, 2, \ldots, N$$

Mass Exchange Between Mobile and Immobile Domains:

$$\theta_{im} \frac{\partial C_i^{im}}{\partial t} + (1 - \theta_{im})\rho_s \frac{\partial q_i^{im}}{\partial t} = \theta_{im}\beta(C_i^m - C_i^{im})$$

Mobile Domain Multi-Rate Equation:

$$\frac{\partial q_i^m}{\partial t} = \int_0^\infty f(\alpha)(Q_i^m - q_i^m)d\alpha \qquad f(\alpha): \begin{array}{l} \text{lognormal} \\ \text{distribution} \end{array} \qquad Q_i^m: \begin{array}{l} \text{From surface} \\ \text{complexation} \end{array}$$

Immobile Domain Multi-Rate Equation:

$$\frac{\partial q_i^{im}}{\partial t} = \int_0^\infty f(\alpha)(Q_i^{im} - q_i^{im})d\alpha \qquad f(\alpha): \begin{array}{l} \text{lognormal} \\ \text{distribution} \end{array} \qquad Q_i^{im}: \begin{array}{l} \text{From surface} \\ \text{complexation} \end{array}$$

➤ Total site density was calculated based on the mass weight of the reactive size fraction in the large column;

➤ Sorbed U(VI) was splitted in mobile and immobile domains based on their porosity values.

Parameters in Modeling U(VI) Desorption in Column Experiments

Parameters	Symbol	Unit	SC-1	SC2	LC
Column Length	L	cm	10.5	10.5	80
Pore velocity	v	cm/h	8.60	7.75	3.52
Dispersion coefficient	D	cm2/h	15.25	3.64	46.52
Porosity	θ	/	0.41	0.46	0.32
Soil bulk density	ρ_b	kg/L	1.56	1.42	1.88
Immobile porosity	θ_{im}	/	0.00	0.00	0.064
Logarithm mean rate	μ	$\log(h^{-1})$	-9.99	-9.99	-9.99
Standard deviation	σ	$\log(h^{-1})$	2.66	2.66	2.66

Two domain mass exchange rate constant (h^{-1})	PFBA	Tritium	Br	U(VI)
	1.45×10^{-2}	4.28×10^{-2}	3.87×10^{-2}	1.45×10^{-2}