# Inverse Modeling of Experiments to Support More Realistic Simulation of Sorbing Radionuclide Transport

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## Introduction

Between 2008 and 2010, a series of adsorption, desorption, and column transport experiments were conducted to evaluate the transport of U and Np through saturated volcanic tuffs. Data were collected on effluent concentrations and residual sorbed concentrations on the column. Experimental results are interpreted using a conceptual and numerical model that accounts for kinetic sorption on several different types of sites (varying from weak to very strong).

Model calibration and uncertainty analysis were implemented using the PEST software code, including an augmentation of the null space Monte Carlo method using the Latin hypercube sampling algorithm. Optimization methods result in a best fit to experimental data. Formal uncertainty quantification methods provide an assessment of data worth and the identifiability of model parameters. Both linear and nonlinear analytical techniques were applied in the uncertainty analysis.

## Experimental Setup

Samples consisted of ash-flow tuff from borehole UD-25c#2 and water was from well J-13 at the Nevada Test Site. Batch sorption and desorption experiments were conducted on crushed tuff in flow-through reactor cells (see photo at left).

Column transport experiments were conducted for two different flow rates (7 ml/hr and 28 ml/hr) for U. Breakthrough concentrations were measured, as well as sorbed concentrations in frozen, sectioned columns to obtain post-mortem profiles. Combined information provided a unique and complex picture of radionuclide transport.

## Numerical Model

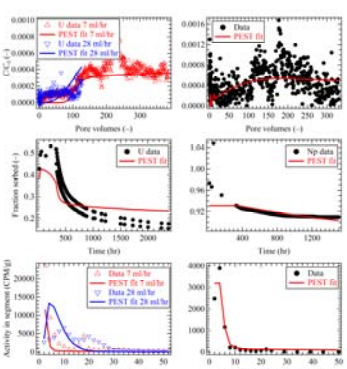
$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{1}{V_\mathrm{T}}\left\{Q\left(C_{in} - C\right) - \left[\sum_{i=1}^{4} k_{f_i}\left(1 - \frac{s_i}{s_{i_\mathrm{max}}}\right)\right]C + \sum_{i=1}^{4} k_{r_i} s_i\right\},$$

$$\frac{\mathrm{d}s_i}{\mathrm{d}t} = \frac{1}{M}\left[k_{f_i}\left(1 - \frac{s_i}{s_{i_\mathrm{max}}}\right)C - k_{r_i} s_i\right],$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\left\{\left[\sum_{i=1}^{4} k_{f_i}\left(1 - \frac{s_i}{s_{i_\mathrm{max}}}\right)\right]C + \sum_{i=1}^{4} k_{r_i} s_i\right\},$$

| | |
|---|---|
| $C$ | concentration out of reaction vessel, CPM/mL or mol/mL |
| $C_{in}$ | concentration in solution flowing into reaction vessel, CPM/mL or mol/mL |
| $s_i$ | concentration sorbed to site *i*, CPM/g or mol/mL |
| $s_{imax}$ | maximum concentration that can be sorbed to site *i*, CPM/g or mol/mL |
| $V_T$ | volume of solution in reaction vessel, mL |
| $Q$ | flow rate through reaction vessel (zero during sorption phase), mL/hr |
| $M$ | mass of solid, g |
| $k_{fi}$ | forward (adsorption) rate constant for site *i*, mL/g-hr |
| $k_{ri}$ | reverse (desorption) rate constant for site *i*, 1/hr |
| $t$ | time, hr |
| $D$ | solute dispersion coefficient in column, cm$^2$/hr |
| $v$ | mean pore velocity in column, cm/hr |
| $x$ | distance along column, cm |
| $\rho$ | bulk density of tuff in column, g/cm$^3$ |
| $\theta$ | column porosity |

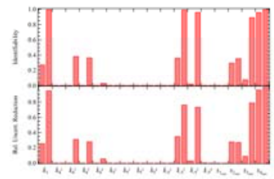
## Experimental Results and Model Calibration



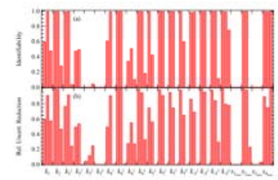

Model calibration was performed simultaneously on the multiple data sets from the experiments using automated optimization. Parameter limits were assigned fairly broadly and weights were assigned as the inverse of the standard deviation in measurement noise of each data point, initially. A hierarchical weighting scheme was adopted in which inter-experimental data were scaled such that each experiment contributed roughly equally to the overall objective function.

## Linear Uncertainty Analysis

Np Parameter Identifiability



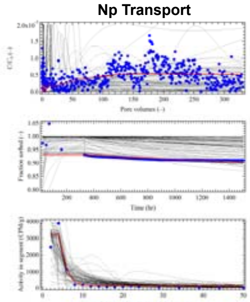
U Parameter Identifiability



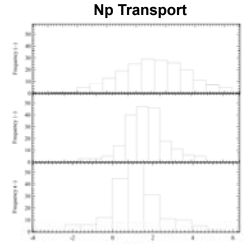
PEST utility GENLINPRED performs generalized linear predictive uncertainty analyses. These analyses include estimates of parameter identifiability and uncertainty reduction (Doherty and Hunt, 2009). Also, it can determine how much a parameter's uncertainty is reduced as a function of each group of data. Identifiability is an indicator of our ability to determine a parameter's value based on the available data set. Uncertainty reduction is the fraction of the parameter range that can be reduced through the calibration process. The two bars for the Np parameters and the three bars for the U parameters correspond to the two and three data sets used in each calibration.

## Nonlinear Uncertainty Analysis

Np Transport



Np Transport



PEST's null space Monte Carlo (NSMC) technique was employed to investigate the nonlinear uncertainties of each parameter. While NSMC is parsimonious with regard to model calls, it was further improved through use of Latin Hypercube Sampling (LHS), which replicates a distribution with fewer random samples using a stratified sampling approach. 100 realizations were drawn for each parameter (34 for Np and 66 for U) from the underlying truncated, lognormal distributions. The resulting forward model runs are shown in the upper plots.

The strength of this analysis is to determine a calibration-constrained distribution of each parameter to yield its full nonlinear uncertainty distribution. The LHS values for the $k_2$ parameter are shown in the upper histogram. The values are "warped" within the null space in the middle plot. Finally, these warped parameters are provided to PEST and recalibrated for a single iteration as shown in the lower plot.

## Conclusions

This exercise has demonstrated a new capability in PEST – using LHS to generate parameter distributions that are first processed with PNULPAR and then by a single NSMC PEST iteration. Full nonlinear uncertainty distributions of each parameter result. Moreover, in the process of obtaining each nonlinear uncertainty distribution, the linearized uncertainty analysis is also obtained – specifically, the identifiability and uncertainty reduction of each parameter. This information also informs us as to how each data set contributes to the uncertainty reduction of each parameter. This is important information because it allows the modeler to tell the experimentalist just how much information is contained in a data set. This data worth information can help design future experiments and specify if more or less of a certain data type should be collected. In this example, the column post-mortem activity data were particularly important, indicating that additional data of this type should be collected.

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