Pacific Northwest NATIONAL LABORATORY

PNNL-36587
DVZ-RPT-114

# Simulation of Particulate Transport for Delivery of Solid Amendments into the Subsurface:

## FY24 Status Report

September 2024

Katherine Muller
Glenn Hammond
Bryan He

U.S. DEPARTMENT of ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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# Simulation of Particulate Transport for Delivery of Solid Amendments into the Subsurface: FY24 Status Report

**September 2024**

*Katherine Muller, Glenn Hammond, Bryan He*

## Summary

For particulate-based amendments to be viable for field-scale remediation at the Hanford Site (e.g., 200-DV-1 Operable Unit), particles need to be delivered a sufficient radial distance from an injection well and retained at concentrations high enough for effective treatment. An accurate description of the particle radius of influence (ROI) is critical for developing an overall remediation strategy. However, field-scale particle simulations are currently limited due to insufficient simulation capabilities and a lack of experimental data to validate and parameterize particle transport models. To help build toward field-scale deployment, this fiscal year (FY) we have (1) developed a pre-screening tool to estimate particle transport, (2) implemented particle transport models within PFLOTRAN, and (3) conducted preliminary estimations of particle ROI.

While field-scale numerical simulations will ultimately be necessary before remedy design and field implementation, we have developed a pre-screening tool that offers valuable estimations of expected particle injectability and ROI in a 1-D system. The advantage of the tool is that it does not require extensive laboratory experiments and instead makes predictions based solely on routine laboratory measurements. This tool can assist in down-selection and decision-making by identifying which particle amendment systems are worth pursuing in future laboratory experiments, such as 1-D column tests and beyond. With any system, scaling up from the lab to the field presents challenges. Currently, there is no field data available for model calibration or validation. However, the theoretical particle models being developed herein are the best tools available to guide progress toward field deployment. To help bridge this gap and verify model predictions, larger-scale lab experiments are being proposed.

To advance simulation capabilities, six particle transport models are being integrated into the reactive transport simulator PFLOTRAN.[1] These include colloid filtration theory (CFT) and five additional particle transport models (M1-M5). Each model, from M1 to M5, progressively incorporates additional particle transport and retention processes. Ultimately, the simplest model capable of accurately describing 1-D column data will be selected and parameterized. During FY24, the CFT and M1 model have been fully implemented within PFLOTRAN. Using an existing 1-D column experiment, the two currently implemented particle transport models (CFT and M1), and associated parameters, were fit to this experiment.

While simpler model formulations are helpful for estimations, these formulations could not fully describe particle transport and retention behavior in the previous 1-D column experiment. Thus, additional complexities will need to be considered, which will be accounted for in the M2-M5 model formulations.

[1] PFLOTRAN: A Massively Parallel Reactive Flow and Transport Model for describing Subsurface Processes (www.pflotran.org)

Additionally, because a viscous, shear thinning fluid was required to keep particles in suspension, considerations for flow will also need to also be accounted for. Therefore, a new immiscible two-phase flow mode is currently being implemented in PFLOTRAN. With some modifications, this new flow module could also support simulation of non-Newtonian liquid amendments, foams, and emulsions.

We also estimated the expected ROI of solid amendments using 1-D simulations. The average predicted ROI was approximately 15 ft for micron-sized zero valent iron (mZVI) suspended in xanthan gum (XG). Using the pre-screening tool and ROI estimates, additional amendment-delivery laboratory characterization and experiments are proposed. The results from additional experiments can be used to validate and parametrize particulate transport model formulations, which will ultimately provide predictive capabilities for field amendment-delivery systems.

## Introduction

Currently, nine technologies are being evaluated for their ability to reduce long-term contaminant mobility in the 200-DV-1 Operable Unit (DOE/RL 2019). Five of these technologies are solid-phase amendments, including stannous apatite, two bismuth-based materials, and two iron-based materials. Laboratory results indicate these particulate amendments hold promise for sequestration of primary and some co-contaminants, but the ability to inject and emplace these materials throughout the subsurface still presents technical challenges (PNNL-35432 2023).

While current laboratory experiments are aimed at evaluating treatment effectiveness, there have been ancillary lessons learned about potential field implementation (e.g., observed plugging and particulate amendment injection distances achieved in 1-D columns). Still, additional testing, evaluation, and simulations are necessary to fully consider aspects related to amendment delivery and implementation at the field scale. Developing tools and simulation capabilities to evaluate the delivery of solid amendments will enable informed decision-making when assessing the feasibility of particulate amendments and choosing associated properties for field-scale implementation.

This progress report describes capability development toward field-scale simulation of particle amendments in PFLOTRAN. This includes the creation of a pre-screening tool for selecting appropriate amendment-delivery fluid systems, the implementation of particle transport models within PFLOTRAN, preliminary parameterization based on a 1-D column experiment, and estimations of the expected ROI.

## Particle Transport Favorability Pre-screening Tool

Amendment particles need to remain in suspension to be successfully injected in the subsurface. Particle suspension stability is a function of particle and fluid properties. By calculating the forces between amendment particles, suspension stability can be estimated (Figure 1). A user-friendly pre-screening tool was developed in a Jupyter Notebook,[2] enabling users to quickly estimate particle suspension stability by categorizing it as very stable, kinetically stable (i.e., stable on the order of hours), or unstable.

[2] Jupyter Notebook (formerly known as IPython Notebook) is a web-based open source application enabling interactive data science and scientific computing across all programming languages (https://jupyter.org/).

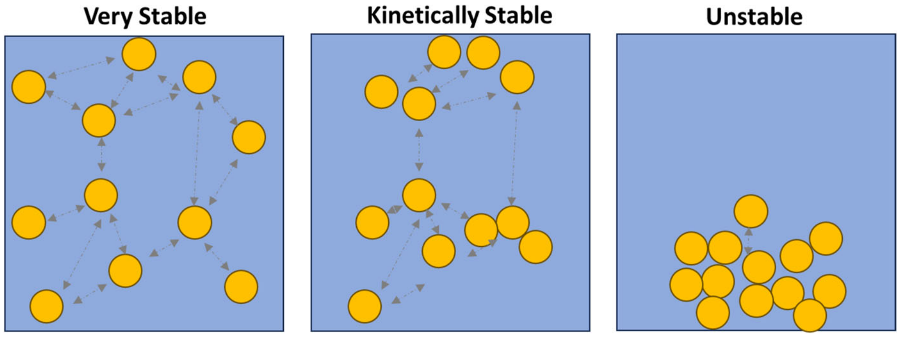


Figure 1. Particle suspension stability: (left) very stable, (middle) kinetically stable, and (right) unstable.

This tool provides real-time information on the expected suspension stability for a given amendment-delivery fluid combination. To improve stability, modifications can be made to the particles (e.g., polymer coating or encapsulation) or the fluid (e.g., using a highly viscous solution such as XG). Such potential modifications can be quickly tested with this pre-screening tool to evaluate the likelihood of improving suspension stability. Given the numerous possible amendment-delivery fluid combinations and concentrations, this tool helps focus laboratory efforts on systems that show promise.

Further, by also including properties of the porous media (e.g., targeted treatment zone in the subsurface), the pre-screening tool can estimate particle transport behavior. Various mechanisms are responsible for the overall accumulation of amendment particulates in porous media (Figure 2). Mechanisms include particle attachment and detachment to the surface of porous media grains, aggregation of individual particles into a larger agglomerate, straining of particles within small pore throats, and blocking of surface sites available for attachment or adsorption.

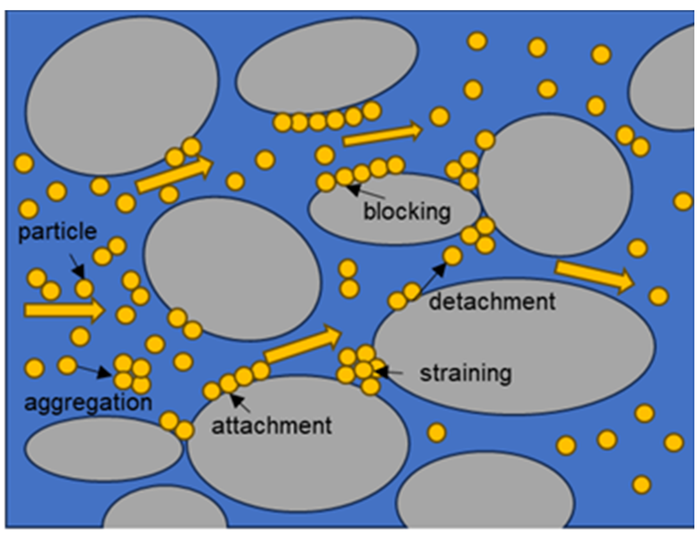


Figure 2. Particle transport and retention mechanisms through porous media (adapted from Yursuf et al. 2024). The transport and retention of particles (yellow circles) through porous media (grey ovals) are influenced by aggregation, attachment and detachment, and blocking and straining mechanisms along the flow path (yellow arrows).

While many mechanisms are active at the pore scale, CFT is frequently used as a simplified model. CFT groups all mechanisms into a single first order deposition rate, $k_d$, to describe overall particle retention. The pre-screening tool calculates the deposition rate, writes the corresponding PFLOTRAN input deck, and runs a 1-D reactive transport simulation with PFLOTRAN to better evaluate the potential particle transport distance.

In general, the smaller the colloid particle size, and the more charged the particles, the greater the anticipated stability and transport distance. Still, system-specific measurements are needed to better constrain particle transport predictions.

## Particle Transport Model Implementation and Verification

CFT and five different particle transport models (M1-M5) are currently being implemented within PFLOTRAN (Table 1). Model complexity increases with model number to include the additional mechanisms described in Figure 2. To date, CFT and M1 have been successfully implemented in PFLOTRAN.

Table 1. Particle Transport Models and PFLOTRAN Implementation Status

| Model | Mechanisms Modeled | Implementation Status |
|---|---|---|
| CFT | Deposition | Complete (FY24) |
| M1 | Attachment with blocking (one site) | Complete (FY24) |
| M2 | Straining with blocking (one site) | In progress (FY25) |
| M3 | Attachment with blocking and straining (one site) | In progress (FY25) |
| M4 | Attachment with blocking and straining (two sites) | In progress (FY25) |
| M5 | Attachment with a maximum surface concentration (one site) | Not started (FY25) |

Each model formulation will be tested for its ability to describe experimental data, starting with the simplest. This assessment will be completed using a previously conducted 1-D flow column experiment where mZVI within an XG delivery fluid was injected. This amendment-delivery fluid formulation is relevant to target the DV-1 area and applications.

CFT and M1 model parameters were fit to the experimental breakthrough curve and retention profile data using the parameter estimation tool PEST: Model-Independent Parameter Estimation and Uncertainty Analysis software (Doherty 2015). Figure 3 shows the best fit model results for the mZVI-XG column experiment. The CFT best fit determined the deposition rate parameter, $k_d$, to be 2.0 $h^{-1}$.

These simpler model formulations could not fully describe particle behavior, suggesting more complex model formulation is required. It is anticipated that a more sophisticated particle transport model will be able to capture behavior, although it may also require simulation of two-phase immiscible flow to account for the viscous nature of the delivery fluid.

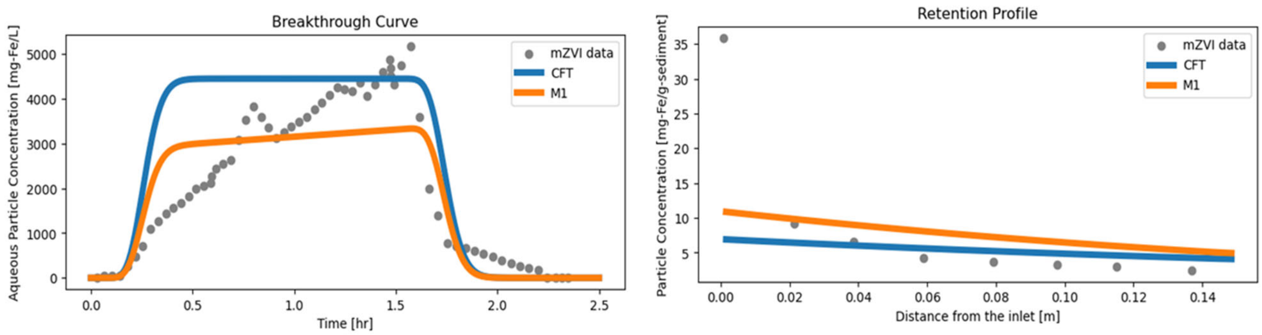


Figure 3. Best fit particle transport model for mZVI-XG 1-D column experiment. Experimental data (grey dots) and simulation results (lines) are shown for the particle breakthrough curve (left) and the particle retention profile (right). The blue line represents CFT model simulation and the orange line represents M1 - attachment with blocking, one-site.

Since mZVI and XG are widely used, we were available to use literature values to predict $k_d$ in the pre-screening tool. The pre-screening calculations estimated $k_d$ to be between 0.48 and 2.2 $h^{-1}$, closely aligning with the more robust and accurate 1-D column fitted $k_d$ value of 2.0 $h^{-1}$. This alignment provides confidence that pre-screening calculations based on easily measurable properties are comparable to CFT model parameters fit to more extensive 1-D column experiment results. However, most of the remedial amendments being considered for the Hanford Site have not been widely used or studied, and thus limited literature values are available for pre-screening predictions. Once measurements (e.g., particle size and zeta potential values) become available for the DV-1 amendments, similar pre-screening calculations will be conducted.

## Radius of Influence Estimation

Forward simulations were conducted to estimate the distance that the mZVI-XG solid phase amendments would travel along a 1-D flow path. Initial amendment concentration and injection pulse duration were varied to provide a range of expected outcomes. The average estimated ROI was around 15 ft, ranging between 13.2 and 16.8 ft when using the parametrized CFT and M1 models, respectively. The input values and parameters need to be better constrained through multi-scale laboratory experiments and characterization to provide more accurate results based on specific conditions for the Hanford Site. These results provide an estimate of the distance that particles can be delivered and the resultant spatial solid phase concentration, which can help inform down-selection to feasible amendment systems. This provides a powerful way to down-select and optimize delivery scenarios, moving more quickly from feasibility evaluation and design to remedy implementation decisions of particulate-based amendments.

## Summary of Proposed Activities

The following simulation capability efforts are planned for FY25:

- Implement particle transport models M2-M5 in PFLOTRAN to better describe 1-D column experiment results.
- Implement two-phase immiscible flow mode in PFLOTRAN to account for the viscous nature of the delivery fluids.
- Build simplified 3-D model of the Hanford 200 Area to simulate particle injections at the field scale.

The following experiments are proposed to support more accurate and representative simulations:

- Measure relevant DV-1 amendments, delivery fluids, and porous media properties required for pre-screening efforts.
- Conduct multi-scale laboratory injection experiments for model verification and parameterization.

## Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory Nuclear Quality Assurance Program (NQAP). The NQAP complies with DOE Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application*, as its consensus standard and NQA-1-2012, Subpart 4.2.1, as the basis for its graded approach to quality. Any data presented in this document is preliminary, For Information Only, and subject to revision. This work emphasized acquiring new theoretical or experimental knowledge. The information associated with this report should not be used as design input or operating parameters without additional qualification.

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