MF6RTM: Flexible Reactive Transport Modeling for Mining Applications via MODFLOW 6 and PHREEQC

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Abstract

Reactive transport modeling is essential for understanding the interplay between hydrogeological processes and chemical reactions in subsurface environments. This study introduces a code coupling MODFLOW-6 and PHREEQC via their respective APIs using a sequential non-iterative approach, providing a modern and open-source coupling that integrates the latest version of both codes. Implemented in Python, the tool is designed for extensibility, uncertainty analysis, and reproducible workflows. The framework handles complex processes including contaminant transport, mineral dissolution, and redox reactions, and is particularly suited to mining environments where coupled hydrogeological and geochemical processes govern metal mobilization and remediation performance, acid and metalliferous drainage migration, and in situ recovery. Its capabilities are demonstrated using an acid mine drainage benchmark problem and compared against PHT3D results.

Keywords: Reactive transport, geochemistry, software

Introduction

Reactive transport modeling is essential for understanding the intricate interplay between hydrogeological processes and chemical reactions in subsurface environments (Prommer *et al.*, 2019). In mining settings, these coupled processes directly influence operational performance and environmental risk by controlling mechanisms such as acid and metalliferous drainage migration, metal mobilization, and contaminant transport, as well as the effectiveness of remediation strategies and in situ recovery operations. Their representation remains challenging due to the complexity of predicting flow, transport, and geochemical interactions across multiple spatial and temporal scales. Therefore, there is a need for integrated and flexible modeling frameworks capable of supporting predictive and decision-relevant analyses in such environments.

Several tools have coupled flow-and-transport simulators with geochemical engines or implemented fully integrated reactive transport solutions. A few actively developed open-source and standalone (implicitly coupled) reactive transport software systems are noteworthy, including CrunchFlow (Steefel, 2014), PFLOTRAN (Hammond, 2022), and OpenGeoSys (Kolditz *et al.*, 2012). Other open-source software has explicitly coupled transport and reaction models, including PHAST (Parkhurst *et al.*, 2010), PHT3D (Prommer *et al.*, 2003), and eSTOMP (Nieplocha *et al.*, 2006). For a more comprehensive overview, see the review by Steefel *et al.*, 2015.

No open software system, however, has ever coupled the current major versions of MODFLOW (v6 released in 2017) and PHREEQC (v3 released 2013). The MODFLOW family of codes remains one

of the most widely used platforms for simulating flow and transport in real-world hydrogeologic applications for exploratory and predictive purposes among researchers and practitioners. Given the number of models and workflows built around MODFLOW, having a robust and modern reactive transport coupling is essential.

Previous couplings with PHREEQC have been developed for MODFLOW-2005/MT3DMS, known as PHT3D (Prommer *et al.*, 2003), and for MODFLOW-USG (Panday *et al.*, 2013), known as PHT-USG. PHT3D has seen extensive use in both academia and practice (Appelo and Rolle, 2010), while PHT-USG has gained traction more recently, particularly among practitioners working with MODFLOW-USG. A key limitation of both approaches is that they require modification of the underlying source code to enable the coupling. This imposes a heavy maintenance burden and increases the risk of the code falling out of date. As MODFLOW 6 and PHREEQC continue to expand in capability and adoption, there is a clear need for a modern, open-source coupling that preserves transparency, extensibility, and computational efficiency.

Here we present MF6RTM, which addresses this need by providing a fully open, Python-based, API-driven integration between MODFLOW 6 and PHREEQC-3 (Parkhurst and Appelo, 2013) using a sequential non-iterative approach (SNIA). This design eliminates custom file-based workflows, reduces opportunities for error, and enables users to construct complex reactive transport simulations directly within reproducible Python workflows. With built-in compatibility with PEST++ (White, 2018) and PyEMU (White *et al.*, 2016), the framework also supports uncertainty analysis, history matching, sensitivity analysis, and multi-objective optimization, providing a flexible and extensible platform for modern reactive transport modeling and collaborative open-source development.

Methods

MF6RTM is implemented in Python and provides a tightly coupled reactive transport workflow by linking MODFLOW-6 and PHREEQC through their respective application programming interfaces, MODFLOWAPI (Hughes *et al.*, 2022) and PHREEQCRM (Parkhurst and Wissmeier, 2015). The numerical solution follows a non-iterative sequential operator splitting approach (Figure 1), in which groundwater flow and solute transport are first solved using MODFLOW 6, followed by geochemical reactions computed using PHREEQCRM. At each transport time step, concentrations simulated by MODFLOW 6 are conditionally passed to PHREEQCRM when the time step is designated as reactive by the modeler, where equilibrium and kinetic reactions are evaluated. The updated chemical states

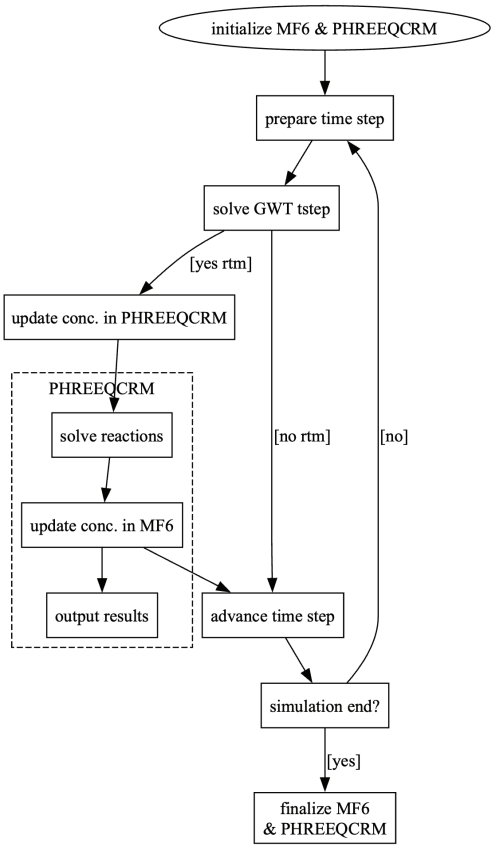

Figure 1 *Schematic of the main solution loop illustrating the sequential operator splitting workflow, including the coupling between flow and transport in MODFLOW 6 and geochemical reactions in PHREEQCRM.*

are then returned to the transport model for the subsequent time step, maintaining tight coupling while allowing flexibility in controlling when reactions are simulated and preserving computational efficiency.

Benchmark and Applied Case

To demonstrate and benchmark MF6RTM capabilities, a mining-relevant reactive transport problem is presented. Originally developed by Walter *et al.*, 1994 and later adopted as a benchmark by Guerin and Zheng (1998), the problem captures key geochemical processes arising when acidic mine tailings leach into an anaerobic carbonate aquifer. Aqueous complexation and dissolution/precipitation are treated as equilibrium reactions. Here we present the 1D benchmark as defined in Walter *et al.*, 1994.

Model Setup

The problem is configured as a 1-dimensional flow and transport domain (column), 0.4 m long, discretized into 80 grid cells. Initial geochemical conditions are summarized in Table 1 and 2. Horizontal hydraulic conductivity was 1 m/day, porosity was 0.35, and longitudinal dispersivity was 0.005 m. Temporal discretization corresponded to a total simulation time of 24 days.

Results

Results are presented in Figure 2 alongside PHT3D simulations, where breakthrough curves for 6, 12, and 24 days are presented. PHT3D (circles) and MF6RTM (lines) are compared, showing good agreement between the two software packages.

The acidic inflow is initially buffered by calcite, maintaining near-neutral pH (6.5–7), during which gypsum precipitates from calcium released by calcite dissolution and sulfate from the inflow. Where calcite is exhausted, siderite becomes the buffering mineral, followed by gibbsite where both are depleted. These three successive buffering mechanisms produce three distinct pH zones and corresponding pe levels, the latter controlled by the Fe^{2+}/Fe^{3+} redox couple, whose concentration ratio, and therefore pe, shifts as mineral buffering evolves and pH declines.

Conclusions

MF6RTM provides a modern, open-source coupling of MODFLOW 6 and PHREEQC that addresses a clear gap in the reactive transport modeling ecosystem. Benchmarking against PHT3D for an acid mine drainage front propagating into a carbonate aquifer demonstrates reliable reproduction of complex geochemical processes, including

Table 1 *Initial and boundary aqueous concentrations (Walter et al., 1994).*

Component	Aquifer conc. (mol L^{-1})	Tailings conc (mol L^{-1})
pH	6.96	3.99
pe	1.67	7.69
CO_3^{2-}	3.94×10^{-3}	4.92×10^{-4}
SO_4^{2-}	7.48×10^{-3}	5.00×10^{-2}
Fe^{2+}	5.39×10^{-5}	3.06×10^{-2}
Fe^{3+}	2.32×10^{-8}	1.99×10^{-7}
Mn^{2+}	4.73×10^{-5}	9.83×10^{-6}
Ca^{2+}	6.92×10^{-3}	1.08×10^{-2}
Mg^{2+}	1.96×10^{-3}	9.69×10^{-4}
Na^{+}	1.30×10^{-3}	1.39×10^{-3}
K^{+}	6.65×10^{-5}	7.93×10^{-4}
Cl^{-}	1.03×10^{-3}	1.19×10^{-4}
Al^{3+}	1.27×10^{-7}	4.30×10^{-3}
Si	1.94×10^{-3}	2.08×10^{-3}

Table 2 Initial mineral concentrations (Walter et al., 1994).

Mineral	Formula	Aquifer conc. (mol L^{-1}) bulk
Calcite	$CaCO_3$	6.30×10^{-3}
Siderite	$FeCO_3$	1.82×10^{-3}
Gibbsite	$Al(OH)_3$	8.81×10^{-4}
Ferrihydrite	$Fe(OH)_3$	6.51×10^{-4}
Gypsum	$CaSO_4{\cdot}2H_2O$	0.0
Amorphous silica	SiO_2	1.42×10^{-1}

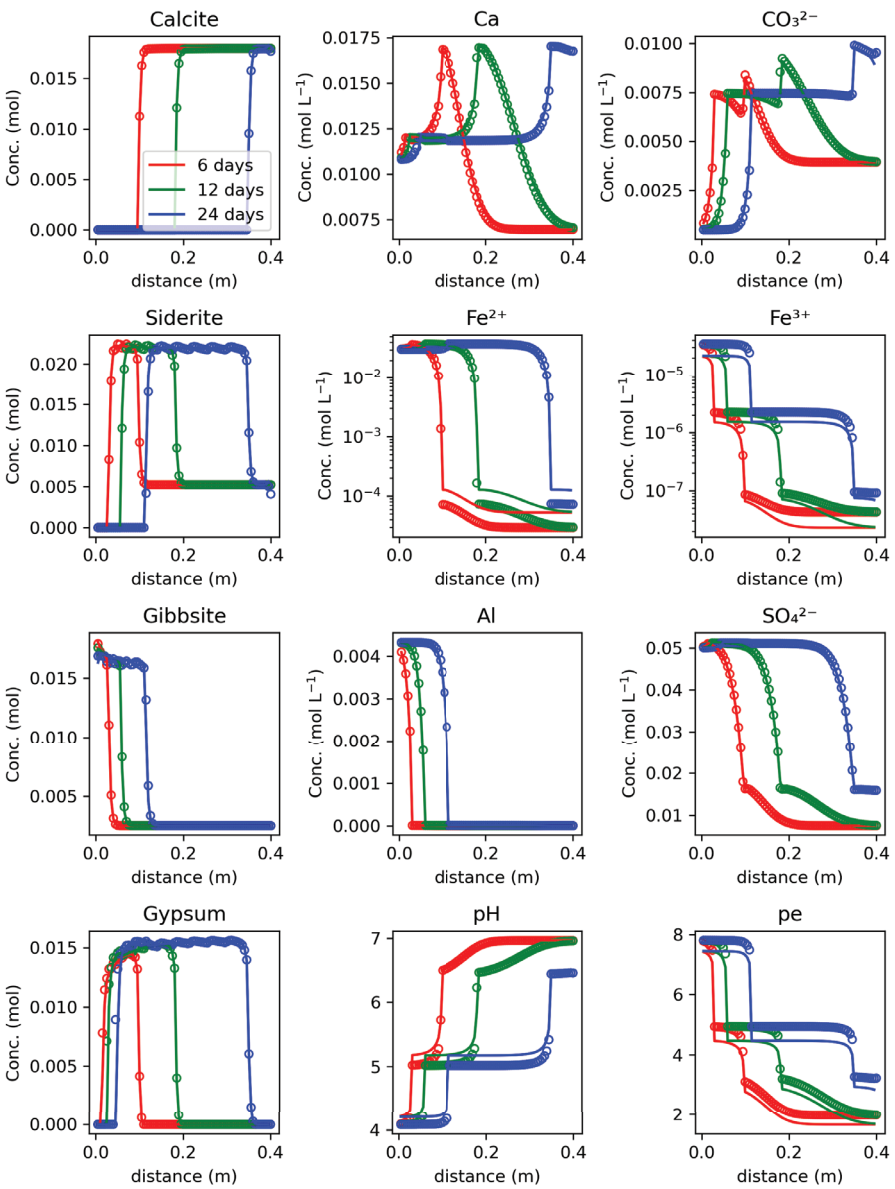

Figure 2 1D benchmark after Walter et al., 1994. Precipitation and dissolution fronts simulated with MF6RTM (lines) compared against PHT3D (circles).

mineral dissolution, precipitation, and redox reactions. The framework is particularly well suited to mining applications, where coupled hydrogeological and geochemical processes govern metal mobilization, acid and metalliferous drainage migration, and remediation and in situ recovery of metals.

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