Comput Geosci (2015) 19:445–478
DOI 10.1007/s10596-014-9443-x

ORIGINAL PAPER

Reactive transport codes for subsurface environmental simulation

C. I. Steefel · C. A. J. Appelo · B. Arora · D. Jacques · T. Kalbacher · O. Kolditz · V. Lagneau · P. C. Lichtner · K. U. Mayer · J. C. L. Meeussen · S. Molins · D. Moulton · H. Shao · J. Šimůnek · N. Spycher · S. B. Yabusaki · G. T. Yeh

Received: 24 April 2014 / Accepted: 26 August 2014 / Published online: 26 September 2014

Abstract A general description of the mathematical and numerical formulations used in modern numerical reactive transport codes relevant for subsurface environmental simulations is presented. The formulations are followed by short descriptions of commonly used and available subsurface simulators that consider continuum representations of flow, transport, and reactions in porous media. These formulations are applicable to most of the subsurface environmental benchmark problems included in this special issue. The list of codes described briefly here includes PHREEQC, HPx, PHT3D, OpenGeoSys (OGS), HYTEC, ORCHESTRA, TOUGHREACT, eSTOMP, HYDROGEOCHEM, CrunchFlow, MIN3P, and PFLOTRAN. The descriptions include a high-level list of capabilities for each of the codes, along with a selective list of applications that highlight their capabilities and historical development.

Keywords Reactive transport · Modeling · Environmental simulation · Computer software · Code benchmark

1 Introduction

In this paper, we present a relatively general description of the mathematical and numerical formulations used in modern numerical reactive transport codes based on

C. I. Steefel (✉) · B. Arora · S. Molins · N. Spycher
Earth Sciences Division, Lawrence Berkeley National Laboratory,
1 Cyclotron Road, Berkeley, CA 94720, USA
e-mail: CISteefel@lbl.gov

C. A. J. Appelo
Hydrochemical Consultant, Valeriusstraat 11, 1071 MB
Amsterdam, the Netherlands
e-mail: appt@hydrochemistry.eu

D. Jacques
Institute for Environment, Health, and Safety, Belgian
Nuclear Research Center, Mol, Belgium

T. Kalbacher · O. Kolditz · H. Shao
Department of Environmental Informatics, Helmholtz Centre
for Environmental Research, Leipzig, Germany

V. Lagneau
University, Centre de Géosciences, 35 rue Saint Honoré,
77305 Fontainebleau Cedex, France

P. C. Lichtner
Lichtner OFM Research, Santa Fe, NM, USA

K. U. Mayer
Earth and Ocean Sciences, University of British Columbia,
Vancouver, Canada

J. C. L. Meeussen
WU Environmental Sciences, University of Wageningen,
Wageningen, the Netherlands

D. Moulton
Mathematical Modeling and Analysis, Los Alamos National
Laboratory, Los Alamos, NM, USA

J. Šimůnek
Department of Environmental Sciences, UC Riverside,
Riverside, CA, USA

S. B. Yabusaki
Earth Systems Science Division, Pacific Northwest National
Laboratory, Richland, WA, USA

G. T. Yeh
National Central University, Jhongli, Taiwan

continuum representations relevant for subsurface environmental simulations. These formulations should be applicable to most of the benchmark problems included in this special issue, although the diversity of formulations and options to be found in the simulators is beyond the scope of a single manuscript. It is felt that the presentation of mathematical and numerical formulations is important, however, so as to avoid the use of either the simulators or the benchmarks as "black boxes". Moreover, a presentation of the formulations gives readers and future users a clearer idea of the limits of the benchmark problems and the model comparisons shown. For example, one expects different results for the benchmark problems using a pore scale rather than a continuum representation, which is the basis for the benchmarks included in this special issue [1–3]. Similarly, the use of a different set of rate laws (e.g., an atomistic rather than a transition state theory formulation) will also most likely produce different results. Thus, the assumption is that the benchmarks presented in the manuscripts that follow are intended for continuum reactive transport simulators that utilize in large part the mathematical and numerical formulations described below. Where important differences in the formulations occur, these are detailed in the individual manuscripts.

This is followed with brief descriptions of the codes used in the benchmarking problems included in this special issue. Again, these descriptions are not exhaustive—the interested reader is referred to the publications cited for the individual codes, or to user's manuals where publication has not been possible. The focus of this special issue is on the presentation of benchmark problems and not the codes themselves. However, we feel it is useful to present at least a brief summary of the capabilities and histories of the various codes now in common use in the environmental simulation community. To first order, this should provide the reader with an idea of which simulators they might want to explore further.

A master set of tables of the subsurface environmental simulation capabilities for each of the codes is also included. Table 1 summarizes the flow and transport capabilities of the codes, while Table 2 summarizes their geochemical and microbial process capabilities. Table 3 provides a short list of the numerical features, including code parallelization, if implemented. The list of continuum-based codes considered here includes PHREEQC, HPx, PHT3D, OpenGeoSys (OGS), HYTEC, ORCHESTRA, TOUGHREACT, eSTOMP, HYDROGEOCHEM, CrunchFlow, MIN3P, and PFLOTRAN. These are many of the most commonly used, widely available reactive transport codes, although others exist. Perhaps more importantly in this context, these are the codes that were used in the benchmark problems included in this special issue. An effort has been made to present a high-level list of capabilities for each of the codes, along with a summary of the historical development that highlights code capabilities first and foremost.

2 Governing equations

2.1 Continuum approach

A rock or sediment or soil mass consisting of aggregates of mineral grains and pore spaces or voids is referred to as a porous medium. An actual porous medium is a highly heterogeneous structure containing physical discontinuities marked by the boundaries of pore walls which separate the solid framework from the void space. Although it is possible, in principle at least, to describe this system at the microscale of individual pores (e.g., [1–3]), such a description rapidly becomes difficult as the size of the system increases and many pore volumes become involved. It is therefore necessary to approximate the system by a more manageable one. One quantitative description of the transport of fluids and their interaction with rocks is based on a mathematical idealization of the real physical system referred to as a continuum. In this theory, the actual discrete physical system, consisting of aggregates of mineral grains, interstitial pore spaces, and fractures, is replaced by a system in which physical variables describing the system vary continuously in space. Allowance is made for the possibility of a discrete set of surfaces across which discontinuous changes in physical properties may occur. In this fictitious representation of the real physical system, solids and fluids coexist simultaneously at each point in space. This is the basis for all of the benchmarks presented in this special issue. Benchmarks for pore scale representations of flow and transport have been presented recently in Oostrom et al. [4].

A representative selection of the most important governing equations for continuum subsurface environmental reactive transport simulators are given below.

2.2 Reaction processes

A range of equilibrium and kinetically controlled biogeochemical reaction processes are typically considered in modern reactive transport simulators, including (1) mineral dissolution and precipitation reactions, (2) homogeneous (aqueous phase) reactions, (3) multisite surface complexation diffuse double layer or triple layer models, with or without an electrostatic correction for the energy associated with charging of the mineral surface, (4) multisite ion exchange reactions, (5) gas–aqueous phase exchange, and (6) microbially mediated homogeneous and heterogeneous
reactions.

2.2.1 Homogeneous phase reactions

Homogeneous or intra-aqueous phase reactions include both classical aqueous complexation reactions, often assumed to be at equilibrium, and kinetically controlled aqueous phase reactions (e.g., microbially mediated sulfate reduction, radioactive decay).

Equilibrium reactions If we assume that the various aqueous species are in chemical equilibrium, it is possible to reduce the number of independent concentrations, that is, the number that actually need to be solved for. Mathematically, this means that in a system containing N_{tot} aqueous species, the number of independent chemical components in the system N_c is reduced from the total number of species by the N_x linearly dependent chemical reactions between them [5–12]. This leads to a natural partitioning of the system into N_c primary or basis species, with concentrations designated here as C_j, and the N_x secondary species, referred to as C_i [8–10]. The equilibrium chemical reactions between the primary and secondary species take the form

$$A_i \rightleftarrows \sum_{j=1}^{N_c} \nu_{ij} A_j \tag{1}$$

where A_j and A_i are the chemical formulas of the primary and secondary species, respectively, and ν_{ij} is the number of moles of primary species j in one mole of secondary species i. The equilibrium reactions provide an algebraic link between the primary and secondary species via the law of mass action for each reaction

$$C_i = K_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_c} \left(\gamma_j C_j\right)^{\nu_{ij}} \quad (i = 1, ..., N_x) \tag{2}$$

where γ_j and γ_i are the activity coefficients for the primary and secondary species, respectively, and K_i is the equilibrium constant for the reaction, written here as the consumption of one mole of the secondary species i. Here, the assumption is that the activities of the species are the product of the species concentrations and their activity coefficients:

$$a_j = \gamma_j C_j \tag{3}$$

This partitioning between primary and secondary species is also used as the basis for the definition of total concentrations, Ψ_j, which are the actual conserved quantities in most of the reactive transport simulators:

$$\Psi_j = C_j + \sum_{i=1}^{N_x} \nu_{ij} C_i. \tag{4}$$

Kinetic reactions When the aqueous phase reactions are kinetically controlled, then the reactions must be written in terms of primary species alone. Treatment of redox disequilibrium is a good example. In this case, the reactions can be written with a transition state theory (TST) type rate law as

$$R_s = k_s \left(1 - \frac{Q_s}{K_{\text{eq}}}\right) \prod a_i^n \tag{5}$$

where k_s is the rate constant for the reaction, Q_s is the ion activity product defined by

$$Q_s = a_i^{-1} \prod_{j=1}^{N_c} a_j^{\nu_{ij}}, \tag{6}$$

where a_j and a_i are the activities of the primary and secondary species in the reaction, and the assumption is that the secondary species, i, has a stoichiometric coefficient of 1 on the left side of the reaction. In addition, the product of various species (the number of which depends on the particular system) affecting the rate far from equilibrium (e.g., H^+) is included as the last term in Eq. 5, with n representing the exponential dependence on the catalytic or inhibitory species. Alternatively, the reaction can be treated as completely irreversible, in which case there is no “affinity” or free energy term $(1 - Q_s/K_{\text{eq}})$:

$$R_s = k_s \prod a_i^n \tag{7}$$

This more general form of irreversible reactions is not limited by any thermodynamic equilibrium constraints and can be used, for example, to model decay and ingrowth of radioactive daughter products.

2.2.2 Gas reactions

Reactions with a discrete gas phase can be included with either an equilibrium or kinetic treatment. In the equilibrium case, mass action equations are similar in form to those for the aqueous complexes, except insofar as the definitions of concentration and activity corrections change. The fugacity of a gas species can be written as

$$f_l = K_l^{-1} \prod_{j=1}^{N_c} \left(\gamma_j C_j\right)^{\nu_{lj}}, \tag{8}$$

where f_l is the fugacity of the lth gas. The fugacity of the gas is related to the partial pressure of the gas through the fugacity coefficient, φ_l:

$$P_l = \frac{f_l}{\phi_l}. \tag{9}$$

In some cases, the assumption of an ideal gas is valid, in which the concentration of the gas species is calculated from the ideal gas law:

$$\frac{n_l}{V} = \frac{P_l}{RT} \tag{10}$$

where n_l and P_l are the number of moles and partial pressures of the lth gas.

2.2.3 Surface complexation

The treatment of surface complexation models in modern reactive transport simulators is now standard, essential in the view of many because it allows for the treatment of sorption as influenced by variable chemical conditions [13, 14]. In this approach, the sorbing sediment surfaces are considered to possess surface functional groups that can form complexes analogous to the formation of aqueous complexes in solution. These surface reactions include proton exchange, cation binding, and anion binding via ligand exchange at surface hydroxyl sites (represented here as XOH). For example, the sorption of a metal could be represented as

$$\mathrm{X{\bullet}OH + M^{z+} \rightleftarrows X{\bullet}OM^{z+\text{-}1} + H^{+}}, \tag{11}$$

where z+ is the valence of the metal. The mass action equation for this reaction is given by

$$K_{\mathrm{eq}} = \frac{[X{\bullet}OM^{\mathrm{z+}\,-\,1}][\mathrm{H}^{+}]}{[X{\bullet}OH][M^{\mathrm{z+}}]}. \tag{12}$$

where the square brackets, [], refer to activities. In Eq. 12, K_{eq} is the equilibrium constant, which in the case of the electrostatic models described below is corrected further for the free energy of surface ionization [15], while the concentrations of the surface complexes are typically written in terms of mole fractions or coverage fractions [14, 16].

It is possible to consider either an electrostatic model in which Coulombic forces associated with charging of the surface are used to correct the equilibrium constant, or a non-electrostatic model in which surface charge (whether present or not) is not used. Non-electrostatic surface complexation is usually implemented based on the generalized composite model where it is assumed that it can be described in terms of "generic" surface functional groups [17]. In the case of the electrostatic surface complexation model in which the electrical double layer (EDL) consisting of an electrical potential that decreases rapidly away from the charged mineral surface is accounted for, the free energy associated with the electrical potential, ΔG_{coul}, is added to the intrinsic free energy associated with chemical bonding, ΔG_{intr}

$$\begin{aligned} \Delta G_{\mathrm{ads}} &= \Delta G_{\mathrm{intr}} + \Delta G_{\mathrm{coul}} \\ &= \Delta G_{\mathrm{intr}} - zF\psi_0 \end{aligned} \tag{13}$$

and ψ_0 is the mean surface potential (V). The equilibrium constant thus can be adjusted for the electrostatic effects according to

$$K_{\mathrm{eq}} = K_{\mathrm{int}} \exp\left(\frac{zF\psi_0}{RT}\right) \tag{14}$$

where K_{int} is the intrinsic equilibrium constant that does not depend on the surface charge.

Kinetic treatments of surface complexation are becoming more common, particularly as it is observed that the equilibrium treatments cannot capture the slow release of metals or contaminants noted in natural soils and aquifers [18].

2.2.4 Ion exchange

Ion exchange reactions can be described via a mass action expression with an associated equilibrium constant [19–22]. The exchange reaction can be written in generic form, assuming here a chloride solution, as

$$v\mathrm{ACl}_u(\mathrm{aq}) + u\mathrm{B}X_v(\mathrm{s}) \leftrightarrow u\mathrm{BCl}_v(\mathrm{aq}) + v\mathrm{A}X_u(\mathrm{s}) \tag{15}$$

where X refers to the exchange site occupied by the cations A^{u+} and B^{v+}. The equilibrium constant or selectivity coefficient, K_{eq}, for this reaction can be written as [18]

$$K_{\mathrm{eq}} = \frac{[\mathrm{BCl}_v]^u\,[\mathrm{A}X_u]^v}{[\mathrm{ACl}_u]^v\,[\mathrm{B}X_v]^u} \tag{16}$$

where the brackets, [], refer to the thermodynamic activities. Several activity conventions are commonly incorporated in modern reactive transport simulators. One possibility is the Gaines–Thomas activity convention, which assumes a reaction stoichiometry of the following form [21], written here for the case of Na^{+} and Ca^{2+} exchange:

$$\mathrm{Na}^{+} + {}^{1}\!/_{2}\mathrm{Ca}X_2 \leftrightarrow \mathrm{Na}X + {}^{1}\!/_{2}\mathrm{Ca}^{2+} \tag{17}$$

where X refers to the exchange site. In the Gaines-Thomas convention, each exchange site, X, has a charge of -1 and the activities of adsorbed species correspond to the charge equivalent fractions. The Gapon activity convention is obtained by writing the reactions in every case with a single exchanger [21]. Alternatively, the Vanselow convention [19] describes the exchanger activity with mole fractions.

2.2.5 Mineral dissolution and precipitation

Minerals may be treated as at equilibrium in a similar fashion to the aqueous complexes, although unless colloidal, they are considered as immobile. Including the mineral concentrations, C_m, in the total component concentrations yields:

$$\Psi_j = C_j + \sum_{i=1}^{N_x} \nu_{ij} C_i + \sum_{k=1}^{N_m} \nu_{kj} C_m \tag{18}$$

Alternatively, mineral dissolution and precipitation can be treated kinetically, which is often an acceptable practice since mineral–water rates are generally much slower than intra-aqueous reaction rates. Local equilibrium behavior is possible by using sufficiently large rate constants, of course—in all cases, the kinetic treatment of reactions is the more general [12]. The types of mineral reactions can be divided into (1) TST type reactions (linear or nonlinear) in which dissolution and precipitation are treated as reversible at equilibrium such that a dependence on Gibbs energy or saturation state is explicitly included, (2) irreversible reactions that include a dependence on Gibbs energy or saturation state, (3) irreversible reactions in which a Gibbs energy or saturation state dependence is not included, although a dependence on concentration can be, and (4) microbially mediated reactions treated with a combination of thermodynamic and kinetic (Monod) terms.

Transition state theory rate laws A general (linear and nonlinear) form for the TST type rate laws for mineral dissolution and precipitation [23, 24] is given by

$$\begin{aligned} R_m &= \mathrm{sgn}\,[\Omega]\, A_m k_m \left(\prod a^n\right) \left|\exp\left(\frac{\eta\,\Delta G}{R\,T}\right) - 1\right|^m \\ &= \mathrm{sgn}\,[\Omega]\, A_m k_m \left(\prod a^n\right) \left|\left(\frac{Q_m}{K_{\mathrm{eq}}}\right)^{\eta} - 1\right|^m \end{aligned} \tag{19}$$

where $\mathrm{sgn}\,[\Omega] = \mathrm{sgn}\left[\log\left(Q_m/K_m\right)\right]$ gives the sign of the reaction term, negative for dissolution, positive for precipitation, A_m is the reactive surface area of the reacting mineral ($\mathrm{m}^2\ \mathrm{m}^{-3}$ porous medium), k_m is the rate constant ($\mathrm{mol\ m}^{-2}\ \mathrm{s}^{-1}$), and the term $\prod a^n$ is product of all of the far from equilibrium effects on the reaction (e.g., pH) that may be catalytic or inhibitory (this is the product over all species, with the assumption of a zero exponent if there is no effect on the reaction rate). Q_m and K_{eq} are the ion activity product and equilibrium constant, respectively. The parameter n can be interpreted as the reaction order, but it may be a non-integer value determined experimentally because of the complicated reaction mechanisms in play. The last term on the right hand side is referred to as the "affinity term" and gives the dependence of the rate on Gibbs energy or saturation state, with η and m representing experimentally or theoretically determined exponential dependences. For example, η can be thought of as the inverse of the Temkin coefficient, which relates the stoichiometric coefficient for the species in the rate-limiting reaction to its stoichiometric coefficient in the mineral.

Dissolution-only or precipitation-only mineral rate laws In Eq. 19, the assumption is that the reaction can be reversed at equilibrium, with a continuous rate between dissolution and precipitation. Another possibility is to use the same rate equation, but as applied to dissolution alone or precipitation alone. This could be the approach in the case of a dissolution rate law that is not continuous on either side of equilibrium (supersaturated or undersaturated) point, that is, the form of the dissolution and precipitation rate laws are not the same. Or it may be possible that there is no or an extremely slow reverse reaction, as appears to be the case for the mineral quartz at 25 °C. In this case, the rates are given by

$$\begin{aligned} R_m &= \mathrm{sgn}\,[\Omega]\, A_m k_m \left(\prod a^n\right) \left[\exp\left(\frac{\eta\,\Delta G}{R\,T}\right) - 1\right]^m; \\ &\qquad \Delta G < 0 \\ R_m &= 0; \quad \Delta G > 0. \end{aligned} \tag{20}$$

This kind of rate law or combination of rate laws can present problems for the reactive transport simulators, since the derivative of the reaction rate that goes into the Jacobian (matrix of function derivatives) is not continuously differentiable.

Irreversible mineral rate laws Alternatively, it is possible to consider irreversible reactions (i.e., those with no affinity or ΔG dependence), with or without a dependence on species concentration or activity

$$R_m = A_m k_m \left(\prod a^n\right), \tag{21}$$

although the thermodynamic basis for such rate laws is less clear, and implementation may result in reactions proceeding past their thermodynamic equilibrium point.

2.2.6 Microbially mediated mineral rate laws

Microorganisms play a critical role in many subsurface environments, in particular, where bioremediation is considered for immobilization of redox-sensitive contaminants by amendment with organic substrates. Microorganisms obtain energy for growth and maintenance from redox reactions. Microbially mediated redox reactions involve two pathways, a catabolic pathway used for energy production and an anabolic pathway used for cell synthesis, the sum of which is the overall stoichiometry of the microbially mediated reaction [25]:

$$0 = \sum_{k}^{N_c} \left(f_s^0 \nu_{jk}^s + f_e^0 \nu_{jk}^e\right) A_k \tag{22}$$

in which ν_{jk}^s and ν_{jk}^e refer to the stoichiometric coefficients for the anabolic (cell synthesis) and catabolic (energy) pathways, respectively, and A_k refer to the species involved in the reactions. The portion of electron equivalents used for cell synthesis ($0 < f_s^0 < 1$) is an input parameter that defines the growth yield of the reaction. The remaining portion of electron equivalents ($f_e^0 = 1 - f_s^0$) defines its energy yield.

The rate of microbially mediated reactions can be written as a function of its maximum intrinsic rate ($\mu_{\max}$, in units of mol per biomass per time), the biomass concentration (B), kinetic limitations ($0 < F_K < 1$) and thermodynamic limitations ($0 < F_T < 1$)

$$R_m = \mu_{\max} B F_K F_T \tag{23}$$

Kinetic limitations are obtained using Monod terms for electron donor (E_D) and acceptor (E_A)

$$F_K = \left(\frac{[E_D]}{K_{E_D} + [E_D]}\right)\left(\frac{[E_A]}{K_{E_A} + [E_A]}\right) \tag{24}$$

Thermodynamic limitations affect the overall rate at low substrate concentrations or for low-energy yielding reactions [26]

$$F_T = \max\left[0, \left(1 - \exp\left(\frac{\Delta G_r + m\Delta G_{\mathrm{ATP}}}{\chi RT}\right)\right)\right] \tag{25}$$

with $m\Delta G_{\mathrm{ATP}}$ being a minimum energy barrier, or energy quantum, that organisms must overcome to catalyze the reaction.

2.3 Fluid flow

2.3.1 Single phase flow

The equation for fluid continuity in the case of single phase flow is given by [27]:

$$\frac{\partial\left[\phi\rho_f\right]}{\partial t} = \nabla\cdot\left[\rho_f \mathbf{q}\right] + \rho_f Q_a \tag{26}$$

where $\nabla\cdot$ is the divergence operator, $\mathbf{q}$ is the volumetric flux (or Darcy flux) of water [m^3 H$_2$O m^{-2} medium s^{-1}], ϕ is the porosity [m^3 void m^{-3} medium], ρ_f is the fluid density [kg m^{-3} H$_2$O], Q_a is volumetric source term [m^3 H$_2$O m^{-3} medium s^{-1}], and t is time [s]. This is a general formulation that is applicable to variable density flow involving a single phase. Single phase flow in permeable subsurface porous media is typically described with Darcy's law [27, 28]. The volumetric or Darcy flux is defined in terms of the fluid pressure gradient:

$$\mathbf{q} = \phi\mathbf{v} = -\frac{\mathbf{k}_{\mathbf{sat}}}{\mu}\left[\nabla P - \rho_f g e_z\right], \tag{27}$$

where $\mathbf{v}$ is the pore velocity [m s^{-1}], z is the depth [m], ∇P [kg m^{-1} s^{-2}, or Pa m^{-1}] is the fluid pressure gradient, g is the acceleration due to gravity [m s^{-2}], and $\mathbf{k}_{\mathrm{sat}}$ [m^2], e_z is a unit vector in the vertical direction, and [m^2] μ [kg s^{-1} m^{-1}] are the permeability tensor for fully saturated conditions and dynamic viscosity, respectively. Alternatively, one can recast the equations in terms of the hydraulic head, h [m], although this is strictly applicable only to isopycnic ("iso-density") flow:

$$h = z + \frac{P}{\rho_f g}. \tag{28}$$

One can also define the hydraulic conductivity tensor, $\mathbf{K}$ [m s^{-1}], as

$$\mathbf{K} = \frac{\mathbf{k}_{\mathbf{sat}}\rho_f g}{\mu}. \tag{29}$$

Written in terms of the hydraulic conductivity and head, Darcy's Law is given by

$$q = -\mathbf{K}\nabla h. \tag{30}$$

2.3.2 Variably saturated flow

Variably saturated flow is typically described either with the full set of multiphase flow and conservation equations, or with the use of the Richards equation, which assumes a passive air phase.

Richards equation Variably saturated flow can be treated using Richards equation [29, 30] under the assumption of a passive air phase and neglecting hysteresis:

$$S_a S_s \frac{\partial h}{\partial t} + \phi\frac{\partial S_a}{\partial t} = \nabla\cdot\left[k_{\mathrm{ra}}\mathbf{K}\nabla h\right] + Q_a, \tag{31}$$

where S_a [m^3 H$_2$O m^{-3} void] defines the saturation of the aqueous phase, S_s[m^{-1}] is the specific storage coefficient and k_{ra} [−] is the relative permeability. The equivalent expression written in terms of pressure is

$$\frac{\partial\left[S_a\phi\rho_f\right]}{\partial t} = \nabla\cdot\left[-\rho_f\frac{k_{\mathrm{ra}}k_{\mathrm{sat}}}{\mu}\left(\nabla P - \rho_f g e_z\right)\right] + \rho_f Q_a. \tag{32}$$

Multiphase flow The component conservation equations for the most general case of multiphase flow can be written for each component j in phase α:

$$\frac{\partial\left[\phi\sum_\alpha \rho_\alpha S_\alpha Y_{j\alpha}\right]}{\partial t} = \nabla\cdot\left[-\sum_\alpha \rho_\alpha Y_{j\alpha}\frac{k_{\mathrm{ra}}k_{\mathrm{sat}}}{\mu}\left(\nabla P - \rho\alpha g e_z\right)\right] + \rho_\alpha Q_j \tag{33}$$

where $Y_{j\alpha}$ is the mass fraction of component j in phase α and the variables are as defined above, except for the more general case of phase α. Thus, a component like CO$_2$ or H$_2$O can be tracked between the various phases, gas, liquid, and solid.

Relative permeability and saturation formulations The relative permeability and aqueous phase saturation can be calculated using the soil hydraulic functions based on van Genuchten [31]:

$$S_a = S_{\mathrm{ra}} + \frac{1 - S_{\mathrm{ra}}}{(1 + \alpha\psi_a^n)^m} \tag{34}$$

$$k_{ra} = S_{ea}^l \left[1 - \left(1 - S_{ea}^{1/m}\right)^m\right]^2 \tag{35}$$

$$S_{\mathrm{ea}} = \frac{S_a - S_{\mathrm{ra}}}{1 - S_{\mathrm{ra}}} \tag{36}$$

where S_{ra} [−] defines the residual saturation of the aqueous phase, ψ_a is the pressure head [m] α[m^{-1}], and n, m, and l are soil hydraulic function parameters, with $m = 1 - {}^1\!/_n$. S_{ea} is the effective saturation of the aqueous phase. The effective saturation of the aqueous phase can also be related to the capillary pressure, P_c [Pa] [31]:

$$S_{\mathrm{ea}} = \left[1 + (\alpha\,|P_c|)^n\right]^{-m}. \tag{37}$$

Other formulations for capillary pressure and aqueous phase saturation are available, e.g., the Brooks–Corey curve [32]:

$$S_{\mathrm{ea}} = \left(\frac{|P_c|}{P_e}\right)^{\lambda} \tag{38}$$

where P_e is the entry pressure [Pa] and λ is a fitting parameter. For the gas phase, the following formulation for relative permeability has been suggested:

$$k_{\mathrm{rg}} = 1 - k_{\mathrm{ra}}, \tag{39}$$

but a formulation proposed by Luckner et al. [33] is often preferred:

$$k_{\mathrm{rg}} = (1 - S_{\mathrm{eg}})^{1/3}\left[1 - S_{\mathrm{eg}}^{1/m}\right]^{2m} \tag{40}$$

where S_{eg} is defined in terms of the liquid saturation, S_a, and the residual gas saturation, S_{rg}, as

$$S_{\mathrm{eg}} = \frac{S_a}{1 - S_{\mathrm{rg}}}. \tag{41}$$

2.4 Molecular diffusion

The simplest treatment of molecular diffusion is in terms of Fick's first law, which states that the diffusive flux of a species in solution is proportional to the concentration gradient:

$$J_j = -D_j \nabla C_j, \tag{42}$$

where D_j is the diffusion coefficient, which is specific to the chemical species considered as indicated by the subscript j. In the case of diffusion in porous media, it is normally necessary to include a tortuosity correction as well (discussed further below). Integrating the diffusive fluxes over a control volume leads to Fick's second law [27]:

$$\frac{\partial C_j}{\partial t} = -\nabla \cdot \left[J_j\right] = \nabla \cdot \left[D_j \nabla C_j\right], \tag{43}$$

which provides an expression for the change in concentration in terms of the divergence of the diffusive flux.

Fick's law is a strictly phenomenological relationship that is more rigorously treated with the Nernst–Planck equation. The full version of the Nernst–Planck equation can be derived from considering the gradient in chemical potential, μ_j, as the driving force for diffusion:

$$J_j = -u_j C_j \frac{\partial \mu_j}{\partial x} = -\frac{D_j C_j}{RT}\frac{\partial \mu_j}{\partial x} \tag{44}$$

where u_j is the species mobility [28] defined by the following:

$$u_j = \frac{D_j}{RT}. \tag{45}$$

To derive the Nernst–Planck equation, we can use a definition of the chemical potential that includes the explicit contribution of the electrochemical potential:

$$\begin{aligned} \mu_j &= \mu_j^0 + RT \ln a_j + z_j F \psi \\ &= \mu_j^0 + RT \ln\left(\gamma_j C_j\right) + z_j F \psi \end{aligned} \tag{46}$$

where μ_j^0 is the standard chemical potential, F is Faraday's constant, z_j is the species charge, and ψ is the electrical potential. By substituting Eq. 46 into Eq. 44, we obtain the following:

$$J_j = -D_j \nabla C_j - \frac{z_i F}{RT} D_i C_i \nabla \psi - D_j C_j \nabla \ln \gamma_j \tag{47}$$

where T is the absolute temperature, and γ_j is the activity coefficient of the jth species. The first term on the right hand side of Eq. 47 is the Fickian diffusion term. The second term on the right hand side is the gradient in electrostatic potential (sometimes referred to as the electrochemical migration term). The electrical potential may develop gradients due to a number of processes (e.g., the application of an electrical current), but as captured in geochemical transport codes at the present time, this effect typically arises due to the diffusion of charged species at different rates (the diffusion potential). The last term in Eq. 47 is the contribution from gradients in activity coefficients, which is presently treated in only PHREEQC Nernst–Planck equation implemented in modern subsurface reactive transport simulators:

$$J_j = -D_j \nabla C_j - \frac{z_i F}{RT} D_i C_i \nabla \psi. \tag{48}$$

2.5 Tortuosity

Tortuosity is defined as the square of the ratio of the path length the solute would follow in water alone, L, relative to the tortuous path length, it would follow in porous media, L_e [27]:

$$T_L = \left({}^{L}\!/_{L_e}\right)^2 \tag{49}$$

With this formulation, the diffusion coefficient in porous media is given by

$$D_i^* = T_L D_i \tag{50}$$

The diffusive flux, then, is given by

$$J_i^{\text{diff}} = -\phi D_i T_L \nabla C_i = -\phi D_i^* \nabla C_i \tag{51}$$

where D_i^* is the diffusion coefficient for species i in porous media.

Various approaches for calculating diffusion coefficients in porous medium, D_i^*, are in use, with a formulation based on Archie's Law employing an exponential dependence on the porosity, being perhaps the most common:

$$D_i^* = \phi^m D_i \tag{52}$$

where m is the cementation exponent. The pore aqueous and gas phase effective diffusion coefficients, D_{ea} and D_{eg}, are also defined locally based on porosity and saturation following the relationship given respectively by Millington [34]:

$$\begin{aligned} D_{\text{ea}} &= \phi^{1/3} S_a^{7/3} D_{0a} \\ D_{\text{eg}} &= \phi^{1/3} S_g^{7/3} D_{0g} \end{aligned} \tag{53}$$

where D_{0a} and D_{0g} are the free phase diffusion coefficients in the aqueous and gas phases, respectively.

2.6 Mechanical dispersion

Mechanical dispersion is defined as the product of the fluid velocity and dispersivity, α, with longitudinal and transverse components

$$\begin{aligned} D_L &= \alpha_L V_i \\ D_T &= \alpha_T V_i \end{aligned} \tag{54}$$

where V_i refers to the average velocity in the principal direction of flow, and the subscripts L(longitudinal) and T (transverse) refer to the dispersion coefficient parallel and perpendicular to the principal direction of flow, respectively [27]. In tensorial index notation, the dispersion tensor becomes

$$D_{ij} = \alpha_T \overline{V} \delta_{ij} + (\alpha_L - \alpha_T) \overline{V_i V_j} / \overline{V} \tag{55}$$

where $\overline{V}$ is the average velocity magnitude, δ_{ij} is the Kronecker delta, and $\overline{V_i}$ and $\overline{V_j}$ are the velocity magnitudes in the I and J coordinate directions, respectively [27]. Only a few of the reactive transport simulators have considered a full dispersion tensor, since the expressions become complicated when flow is not parallel to the principal coordinate directions of the numerical grid. In addition, cross terms can only be considered in finite element formulations, which have the disadvantage of not being locally mass conservative.

2.7 Reactive transport equations

Combining the transport and biogeochemical reaction network terms results in the reactive transport equation

$$\frac{\partial (\phi S_L C_i)}{\partial t} = \nabla \cdot \left(\phi S_L D_i^* \nabla C_i\right) - \nabla \cdot (\mathbf{q} C_i) - \sum_{r=1}^{Nr} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m - \sum_{l=1}^{N_g} \nu_{il} R_l \tag{56}$$

where the term on the left hand side is the accumulation term, with the porosity and liquid saturation, S_L, multiplied by the concentration yielding units of mole per cubic meter medium per second. The reaction terms are partitioned between aqueous phase reactions, R_r, mineral reactions, R_m, and gas reactions, R_l, all considered as kinetically controlled. Where equilibrium aqueous complexation reactions are present (the usual case), it is possible to define a total concentration, as in Eq. 4, and write the reactive transport equation as

$$\frac{\partial (\phi S_L \Psi_i)}{\partial t} = \nabla \cdot \left(\phi S_L D_i^* \nabla \Psi_i\right) - \nabla \cdot (\mathbf{q} \Psi_i) - \sum_{r=1}^{Nr} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m - \sum_{l=1}^{N_g} \nu_{il} R_l \tag{57}$$

The Fickian treatment of dispersion can be added to Eqs. 56 and 57 in a similar way as Fickian diffusion. The Fickian treatment of diffusion in Eq. 57 can be replaced with the Nernst–Planck equation.

Equations 56 and 57 can be expanded to consider transport in phases other that the liquid by adding the corresponding accumulation and transport terms [35, 36].

2.8 Reaction-induced porosity and permeability change

2.8.1 Porosity changes

Porosity changes in matrix and fractures are directly tied to the volume changes as a result of mineral precipitation and dissolution. The molar volumes of minerals created by hydrolysis reactions (i.e., anhydrous phases, such as feldspars, reacting with aqueous fluids to form hydrous minerals such as zeolites or clays) are often larger than those of the primary reactant minerals; therefore, constant molar dissolution–precipitation reactions may lead to porosity reduction.

The porosity, ϕ, of the medium (fracture or matrix) can be calculated from

$$\phi = 1 - \sum_{m=1}^{N_m} \phi_m \tag{58}$$

where N_m is the number of minerals, and ϕ_m is the volume fraction of mineral m in the rock (m^3 mineral m^{-3} medium). As the volume fraction of each mineral changes due to mineral reactions, the porosity can be recalculated at each time step.

2.8.2 Fracture permeability changes

Fracture permeability changes can be approximated using the porosity change and an assumption of plane parallel fractures of uniform aperture [12]. The modified permeability, k, is then given by

$$k = k_0 \left(\frac{\phi}{\phi_0}\right)^3 \tag{59}$$

where k_0 and ϕ_0 are the initial permeability and porosity, respectively. This law yields zero permeability only under the condition of zero fracture porosity. In most experimental and natural systems, permeability reductions to values near zero occur at porosities significantly greater than zero. This generally is the result of mineral precipitation in the narrower interconnecting fracture apertures. This can be described potentially with a higher-order dependence of the permeability on the porosity, or with a percolation threshold model for the permeability [37].

2.8.3 Matrix permeability changes

Matrix permeability changes can be calculated from changes in porosity using ratios of permeabilities calculated from the Carman–Kozeny relation [27] and ignoring changes in grain size, tortuosity, and specific surface area as follows:

$$k = k_0 \frac{(1-\phi_0)^2}{(1-\phi)^2}\left(\frac{\phi}{\phi_0}\right)^3 \tag{60}$$

The simple cubic law (59) and the Kozeny–Carman (60) porosity–permeability equations may not reflect the complex relationship of porosity and permeability in geologic media that depends on an interplay of many factors, such as pore size distribution, pore shapes, and connectivity [38]. Laboratory experiments have shown that modest reductions in porosity from mineral precipitation can cause large reductions in permeability [39].

2.8.4 Effects of permeability and porosity changes on capillary pressures

Permeability and porosity changes will likely result in modifications to the unsaturated flow properties of the rock. Changes to unsaturated flow properties are approximated by modification of the calculated capillary pressure (P_c) using the Leverett scaling relation [40] to obtain a scaled P_c' as follows:

$$P_c' = P_c\sqrt{\frac{k_0\phi}{k\phi_0}} \tag{61}$$

2.9 Multicontinuum representations

Reliable predictions of flow and transport in fractured porous media are important to address several issues, including groundwater contamination, hydrothermal venting, degradation of concrete, carbon sequestration, and mining and mineralization activities. The existence of fractures and heterogeneity in porous media, which are often hierarchical in nature, has led to the multicontinuum class of models. Some of the commonly used continuum-scale models include (1) equivalent continuum model (ECM) [41]; (2) dual permeability model (DPM), dual or multiporosity model [42, 43], multiple interacting continua approach (MINC) [44], and (3) discrete fracture and matrix model [45]. Among these three commonly used approaches, the dual-continuum approach has been extensively applied in different subsurface environments [46–48]. Broadly speaking, the dual-continuum approach considers two interacting regions, one associated with the less permeable intra-aggregate pore region, or the soil matrix domain, and the other associated with the inter-aggregate pore region, or the fracture domain. In this approach, the REV is partitioned into sub-volumes of each domain such that

$$V_{\mathrm{REV}} = V_f + V_m \tag{62}$$

where V_{REV} refers to the volume of the porous medium, V_f and V_m refer to the volume of the fracture and matrix domains, and subscripts f and m refer to the fracture and matrix domains, respectively. Thus, the porosity of each domain is given by

$$\phi_f = \frac{\phi_f}{V_{\mathrm{REV}}},\ \phi_m = \frac{\phi_m}{V_{\mathrm{REV}}} \tag{63}$$

As expected, these relations can be easily extended to include multiple interacting domains. The dual or multidomain conceptualizations can be distinguished by the different formulations of the governing equations of flow in the fracture domain and/or the different approaches through which the exchange between the fracture and rock matrix (or multiple domains) is established. A review of the different multicontinuum approaches including the governing equations and exchange functions are available elsewhere [49–52].

2.10 Thermal processes

Although thermal processes are not the focus of the benchmarks presented in this special issue, we present the governing equation used in most of the non-isothermal codes that actually solve for the energy balance. One form of the governing equation for energy conservation in a porous medium is given by

$$\frac{\partial}{\partial t}\left[\phi\sum_{\alpha}S_\alpha\rho_\alpha U_\alpha \;+\; (1\;-\;\phi)\,\rho_r c_r T\right] \\ +\nabla\cdot\left[\mathbf{q}_\alpha\rho_\alpha H_\alpha\;-\;\kappa\nabla T\right]=Q_e. \tag{64}$$

In this equation, T refers to temperature and the subscript α represents a fluid phase with Darcy velocity $_\alpha$, density ρ_α, saturation S_α, internal energy $_\alpha$, and enthalpy H_α. The coefficient κ denotes the thermal conductivity of the medium and $_{cr}$ and ρr refer to the specific heat and density of the porous medium. The quantity Q_e denotes a source/sink term. Internal energy and enthalpy are related by the equatio

$$U_\alpha \;=\; H_\alpha \;-\; \frac{p_\alpha}{\rho_\alpha}. \tag{65}$$

Thermal conductivity is often described by the phenomenological relationship given by Somerton et al. [53]

$$\kappa \;=\; \kappa_{\text{dry}} \;+\; \sqrt{S_l}\left(\kappa_{\text{sat}}\;-\;\kappa_{\text{dry}}\right) \tag{66}$$

where κ_{sat} and κ_{dry} are the fully saturated and dry thermal conductivities and S_l is the liquid saturation.

3 Numerical formulations

A complete review of the possible numerical formulations is well beyond the scope of this paper. However, we present here a brief summary of some of the more commonly used approaches, which rely in most cases on Newton–Raphson methods for the nonlinear reaction networks found in modern environmental simulators. Although not considered here, similar approaches to coupling flow, solute transport, and energy equations could be included as well. Typically, these are handled via operator splitting, but global implicit (one-step) approaches are possible.

3.1 Numerical approaches for biogeochemical reactions

The general Newton–Raphson approach is summarized in Steefel and MacQuarrie [54]: a series of typically coupled conservation equations for the primary or component species (4) are solved together with kinetic and equilibrium reaction equations. As described by Steefel and MacQuarrie [54], this could consist of 100 % kinetic reactions, in which case the number of conservation equations equals the number of species in the system. Alternatively, when equilibrium can be assumed for some of the aqueous or surface complexes, or for a mineral phase, the reaction rate can be eliminated and replaced with a mass action equation (2). The algebraic equations can be included together with the N_c conservation equations for evolution of the total primary or component species concentrations (4) as a function of time (t), in which case, the number of equations (differential and algebraic) to be solved still equals the number of species, complexes, and minerals in the system.

$$\frac{1}{\Delta t}\left[C_j+\sum_{i=1}^{N_s}\nu_{ij}C_i+\sum_{m=1}^{N_m}\nu_{mj}C_m\right]^{n+1} \\ -\left[C_j+\sum_{i=1}^{N_s}\nu_{ij}C_i+\sum_{m=1}^{N_m}\nu_{mj}C_m\right]^{n}=0\quad j=1,\cdots N_c \tag{67}$$

$$\log C_i^{n\,+\,1}\;=\;\sum_{i\,=\,1}^{N_s}\nu_{ij}\log\left(\gamma_j C_j^{n+1}\right)\;-\;\log\gamma_i^{n\,+\,1} \\ -\;\log K_i\quad i\;=\;1,\cdots N_s \\ \log C_m^{n\,+\,1}\;=\;\sum_{m\,=\,1}^{N_m}\nu_{mj}\log\left(\gamma_j^{n\,+\,1}C_j^{n\,+\,1}\right) \\ -\log K_m\quad m\;=\;1,\cdots N_m \tag{68}$$

where n and $n\;+\;1$ refer to the present and future time level, respectively, the $\gamma_\imath$'s and $\gamma_\jmath$'s are the activity coefficients for the secondary and primary species, respectively, N_s is the number of secondary species or complexes in equilibrium with the primary or component species, and N_m is the number of minerals treated as equilibrium phases. A similar approach can be taken to include equilibrium surface complexes and gases. In addition, the system can be further partitioned between species or mineral phases linked to equilibrium or kinetically controlled reactions. As shown here, the algebraic mass action equations can be linearized by treating the logarithms of the concentrations as the primary unknowns.

An alternative method is referred to as the direct substitution approach (DSA), which can be used to eliminate the algebraic equations corresponding to the mass action equations. In this case, we obtain a nonlinear set of ordinary differential equations for the unknown concentrations of the primary or component species, written here to include explicitly a set of kinetic reactions involving both aqueous species (intra-aqueous kinetic reactions) and mineral phases:

$$
\begin{aligned}
&\frac{1}{\Delta t}\left[C_j+\sum_{i=1}^{N_s}\nu_{ij}\gamma_i^{-1}K_i^{-1}\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{ij}}\right]^{n+1}-\left[C_j+\sum_{i=1}^{N_s}\nu_{ij}\gamma_i^{-1}K_i^{-1}\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{ij}}\right]^{n}\\
&\quad-\left\{\sum_{s=1}^{N_s}\operatorname{sgn}\left[\log\left({}^{Q_s}/{}_{K_s}\right)\right]\nu_{is}k_s\left|\left(\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{mj}}K_s^{-1}\right)^{\eta}-1\right|^{m}\right\}^{n+1}\\
&\quad-\left\{\sum_{m=1}^{N_m}\operatorname{sgn}\left[\log\left({}^{Q_m}/{}_{K_m}\right)\right]\nu_{im}A_m k_m\left|\left(\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{mj}}K_m^{-1}\right)^{\eta}-1\right|^{m}\right\}^{n+1}=0\quad j=1,\cdots N_c. \qquad (69)
\end{aligned}
$$

Note that in this formulation, an implicit solved at the $n+1$ time level is carried out for both equilibrium and kinetic reactions.

Other approaches are possible in which kinetic and equilibrium reactions are decoupled. This approach allows for the use of free energy minimization routines, for example [54–56].

3.2 Approaches for the reactive transport problem

Modern subsurface environmental reactive transport simulators typically use as many as three different approaches to handle the reactive transport equations numerically. The most common approach is operator splitting of the reaction and transport terms, usually in a sequential non-iterative manner. In this approach, the transport of the conserved quantities (typically the total concentrations) is solved, and this is followed by a node by node reaction solve. In the *sequential iterative approach* (SIA), this sequential solve of the transport and reaction is repeated until convergence is achieved. In the *sequential non-iterative approach* (SNIA), however, only a single solve of the transport and reaction terms is carried out. The other approach, referred to as the *global implicit* or *one-step* method, reaction and transport are solved simultaneously [54, 57].

The chief advantage of the global implicit approach is that, unlike the operator splitting method for the reactive transport problem, one is not restricted to time steps less than the Courant condition. The Courant condition would require that mass not be transported more than a single grid cell in any one time step. Even in the case of a Courant number, Cr = 1 operator splitting errors have been reported [58].

3.2.1 Global implicit approach

In the *one-step* or global implicit approach, the transport and reaction terms are solved simultaneously. One approach would be to solve directly for the total concentrations (the Ψ_J's) in any one iteration and then follow this with a distribution of species calculation to determine the concentrations of the individual species. Another method is based on the DSA and consists of solving simultaneously for the complexation (which are assumed to be at equilibrium), the heterogeneous reactions, and transport terms. This means that the primary species (the C_J's) rather than the total concentrations are the unknowns. Following the notation of Lichtner [59], we can introduce the differential operator

$$L(\Psi_J)=\left[\frac{\partial}{\partial t}(\phi S_L)+\nabla\bullet\left(\mathbf{q}-\mathbf{D}^*\nabla\right)\right]\Psi_J, \qquad (70)$$

and write the governing differential equations in terms of the total component concentrations as

$$L(\Psi_J)=R_J^{\mathrm{min}}+R_J^{\mathrm{aq}}\ (J=1,\ldots,N_c), \qquad (71)$$

where the reaction term R_J^{min} includes only kinetic reactions. Note that in this formulation, the diffusion coefficients are assumed to be the same for all of the aqueous species (both primary and secondary) using a Fickian treatment of diffusion.

We proceed by using Eqs. 70 and 2 to obtain an expression for the total soluble concentration in terms of the primary species alone. Substituting this result into Eq. 71 gives

$$
\begin{aligned}
&L\left[C_j+\sum_{i=1}^{N_s}\nu_{ij}\gamma_i^{-1}K_i^{-1}\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{ij}}\right]\\
&+\sum_{m=1}^{N_m}\operatorname{sgn}[\Omega_m]\,\nu_{im}A_m k_m\left|\left(\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{mj}}K_m^{-1}\right)^{\eta}-1\right|^{m}\\
&+\sum_{s=1}^{N_s}\operatorname{sgn}[\Omega_s]\,\nu_{is}k_s\left|\left(\prod_{j=1}^{N_c}(\gamma_j C_j)^{\nu_{mj}}K_s^{-1}\right)^{\eta}-1\right|^{m}=0\\
&j=1,\cdots N_c, \qquad (72)
\end{aligned}
$$

where $\operatorname{sgn}[\Omega_m]$ and $\operatorname{sgn}[\Omega_s]$ give the sign of the reaction term for the kinetic mineral and aqueous complex reactions, respectively.

3.2.2 Nonlinear solver method for global implicit

Using a global implicit approach becomes more difficult in the case of a multicomponent, multispecies system, both because the coupling of species via reactions enlarges the size of the coefficient matrix and because it typically results in sets of nonlinear equations which must be solved. The size of the Jacobian matrix which must be constructed and solved becomes larger, since each function will include contributions from the concentrations both at that nodal point itself and from neighboring nodal points which are used in the finite difference discretization. For example, in the case of one-dimensional transport and N_c unknown concentrations at each nodal point, the form of the Newton equations to be solved is [12, 54]

$$
\begin{aligned}
&\sum_{k=1}^{N_c}\frac{\partial f_{i,j}}{\partial C_{k,j}}\delta C_{k,j}+\sum_{k=1}^{N_c}\frac{\partial f_{i,j}}{\partial C_{k,j+1}}\delta C_{k,j+1}\\
&\quad+\sum_{k=1}^{N_c}\frac{\partial f_{i,j}}{\partial C_{k,j-1}}\delta C_{k,j-1}=-f_{i,j} \qquad (73)
\end{aligned}
$$

where i refers to the component number, k is the unknown component species number, and j, $j+1$, and $j-1$ are the nodal points. The Jacobian matrix in the case of one-dimensional transport takes a block tridiagonal form

$$
\begin{bmatrix}
A_{1,1} & A_{1,2} & 0 & \cdots & & & \\
A_{2,1} & A_{2,2} & A_{2,3} & \cdots & & & \\
 & & & \cdots & & & \\
 & & & \cdots & A_{N-1,N-2} & A_{N-1,N-1} & A_{N-1,N}\\
 & & & \cdots & 0 & A_{N,N-1} & A_{N,N}
\end{bmatrix}
\times
\begin{bmatrix}
\delta C_1\\ \delta C_2\\ \cdots\\ \delta C_{N-1}\\ \delta C_N
\end{bmatrix}
=-\begin{bmatrix}
f_1\\ f_2\\ \cdots\\ f_{N-1}\\ f_N
\end{bmatrix}
\qquad (74)
$$

where the entries in the Jacobian matrix (the A) are submatrices of dimension N_c by N_c in the case where there are N_c unknowns per nodal point. The entries δC_i refer here to the entire vector of unknown concentration corrections at any particular nodal point, while the functions f_i include the entire vector of equations for the unknown concentrations at each nodal point. In practice, the logarithms of the primary species concentrations are solved for rather than the concentrations themselves, which introduces a natural scaling of the numerical approach that greatly improves convergence properties.

3.2.3 Operator splitting approach

Operator splitting of reaction and transport is an alternative to the global implicit approach [12, 54]. In this approach, a single time step consists of a transport step followed by a reaction step using the transported concentrations. Physically, one can think of the method as equivalent to taking part of the contents of one beaker (i.e., one node) and adding it to a second beaker downstream. After this physical process is completed, reactions occur which modify the chemical composition of each of the beakers in the sequence. Mathematically, the method can be represented as a two step sequential process consisting of a transport step

$$
\frac{\left(C_i^{\mathrm{transp}}-C_i^{n}\right)}{\Delta t}=L(C_i)^n,\quad (i=1,\ldots,N_{\mathrm{tot}}), \qquad (75)
$$

followed by a reaction step

$$
\frac{\left(C_i^{n+1}-C_i^{\mathrm{transp}}\right)}{\Delta t}=R_i^{n+1}\quad (i=1,\ldots,N_{\mathrm{tot}}) \qquad (76)
$$

where L is the spatial operator. The problem can also be formulated using the total concentrations, thus reducing the number of equations which must be solved. In the case where the Courant number is 1, then the entire contents of one grid cell are transferred to the next one downstream, and the approach is equivalent to that of a mixing cell model when explicit time weighting and a formulation without numerical dispersion is used.

4 Code descriptions

The diversity of process models (Section 3) and numerical approaches (Section 4) used in the simulation of reactive transport in subsurface environments makes it nearly impossible for any code to include all potential capabilities or to run on all computer architectures, from workstations to distributed memory parallel systems. Further, code development has typically occurred incrementally over several years, in some cases over a decade or more, driven by the needs of research projects. The reactive transport codes used for this benchmarking effort reflect the heterogeneity resulting from this process; even when re-engineered from the ground up, the codes are the legacy of years of development and research. In some instances, development of native geochemical capabilities from scratch has been circumvented by coupling flow and transport codes, typically using an operator splitting approach, to existing geochemical capabilities. In the code overview that follows, we start with PHREEQC, a geochemical code that is used as geochemical engine in HPx, PHT3D, and OpenGeoSys. HYTEC uses the same concept to bring in the geochemical capabilities of CHESS. We follow with codes that have native geochemical modules. ORCHESTRA is distinctive in that all model definitions are separate from the calculation engine or equation solver. TOUGHREACT and eSTOMP use the operator splitting approach, while HYDROGEOCHEM, CrunchFlow, MIN3P, and PFLOTRAN allow for implicit coupling of transport and biogeochemistry.

4.1 PHREEQC

PHREEQC is a computer program developed by Parkhurst and Appelo designed to perform a variety of aqueous geochemical calculations [60, 61]. Originally a batch-reaction model, the current capabilities of PHREEQC include inverse modeling and one-dimensional transport calculations with a wide range of physical and chemical processes. PHREEQC can simulate a range of equilibrium and kinetic reactions. Several aqueous models are implemented in the databases available for PHREEQC, including ion-association models that use Debye–Hückel formulations (*phreeqc.dat*, *wateq4f.dat*, *llnl.dat*, *minteq.dat*, *minteq.v4.dat*, and *iso.dat*); the Pitzer specific-ion interaction model (*pitzer.dat*), and the specific-ion interaction theory (SIT) model (*sit.dat*). All databases include temperature dependence of activity-coefficient constants and van't Hoff or analytical expressions for equilibrium constants [60].

Heterogeneous equilibria that can be imposed include surface complexation, ion exchange, fixed-composition gases and minerals, solid solutions, and a multicomponent gas phase. Surface complexation can be calculated by using the diffuse-double layer model or the CD-MUSIC model. In addition, it is possible to calculate explicitly the composition of the diffuse layer that balances the charge accumulated by surface complexation. Solid solutions may be ideal-multicomponent or nonideal-binary solid solutions.

The *pitzer.dat* and *phreeqc.dat* databases have additional features. Density and specific conductance are calculated as functions of the solution composition. Molar volumes of aqueous species are calculated as functions of pressure, temperature, and ionic strength, which allow calculation of the pressure dependence of equilibrium constants [62]. These databases use the Peng–Robinson formulation for nonideal gas fugacities and can provide accurate simulations of mineral and gas solubilities up to 200 °C and 1,000 bar for major elements [62]. It may be noted that the calculation of density-driven flow requires composition, temperature, and pressure-dependent solution densities such as calculated by PHREEQC. The *iso.dat* database implements an approach to isotopes where each isotope is considered to be a separate thermodynamic component [63]. The database allows simulation of kinetic and equilibrium fractionation of isotopes of carbon, hydrogen, nitrogen, oxygen, and sulfur and can be extended to other isotopes.

Homogeneous or heterogeneous kinetic reactions can be defined with arbitrary rate expressions that are functions of solution composition and availability of solid reactants by using Basic programs that are evaluated with an embedded Basic interpreter. The general kinetic reaction capability of PHREEQC can be used for any biological reactions. It is possible to formulate any rate expression, including Monod or kinetics of any order, inhibition factors, rates that depend on free energy, and rate variation as a function of available electron acceptors. It is also possible to consider the effects of a consortium of bacteria that have specific substrate requirements and individual rates of consumption, growth, and decay.

Solute-transport calculations may consist of advection and dispersion or pure diffusion. Advection is simulated with the maximal time step allowed by the Courant criterion, while dispersion is simulated with sub-time steps when required by the Von Neumann criterion. Reactions are calculated after each advective and dispersive step. The method can accurately simulate advective–dispersive systems and can propagate a square wave with no numerical dispersion for unretarded solutes. In diffusive calculations, a single diffusion coefficient can be used for all aqueous species, or individual diffusion coefficients can be used for each aqueous species subject to the constraint of no net transport

Table 1 A comparison of the key flow and transport features of reactive transport modeling codes

Capabilities/features	PHREEQC	HP1/HPx	PHT3D	OpenGeoSys	HYTEC	ORCHESTRA	TOUGHREACT	eSTOMP	HYDROGEOCHEM	CrunchFlow	MIN3P	PFLOTRAN
Dimensions	1D	1,2,3D	1,2,3D	1,2,3D	1,2,3D	1D	1,2,3D	1,2,3D	1,2,3D	1,2,3D	1,2,3D	1,2,3D
Flow												
Saturated flow	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Richards equation	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes
Multiphase–multicomponent flow	No	No	No	No	Yes	No	Yes	Yes	Yes	No	No	Yes
Variable density flow	No	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	No
Non-isothermal flow	No	No	No	Yes	No	No	Yes	Yes	Yes	No	Yes	Yes
Transport												
Advection	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Molecular diffusion	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Electrochemical migration	Yes	No	No	No	No	Yes	No	No	No	Yes	Yes	No
Dispersion tensor	Diagonal	Diagonal	Diagonal	Diagonal	Diagonal	Diagonal	No	Diagonal	Full	Diagonal	Diagonal	Diagonal
Gas phase advection	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Gas phase diffusion	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Colloids	Yes	No	No	Yes	Yes	Yes	Yes	No	Yes	No	No	Yes
Multiple continua	Yes	Yes	No	Yes	Yes	Yes	Yes	No	No	Yes[a]	Yes[b]	Yes

[a] Not available in CrunchFlow, but available in CrunchFlowEDL

[b] Not available in MIN3P-THCm, but dual porosity model is available in MIN3P-Dual [203]

Table 2 A comparison of the key geochemical and microbial features of reactive transport modeling codes

Capabilities/ features	PHREEQC	HP1/HPx	PHT3D	OpenGeoSys	HYTEC	ORCHESTRA	TOUGHREACT	eSTOMP	HYDROGEOCHEM	CrunchFlow	MIN3P	PFLOTRAN
Geochemistry												
Extended Debye-Hückel	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes
Davies activity model	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	No
Pitzer activity model	Yes	Yes	No	Yes[a]	No	No	No	Yes	No	No	Yes	No
Non-isothermal geochemistry	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Surface complexation[b]	DDL, Non-edl	DDL, Non-edl	DDL, Non-edl	DDL, Non-edl	DDL, CC	DDL	DDL, CC	DDL, Non-edl	DDL, Non-edl	DDL, Non-edl	Non-edl	Non-edl
Ion exchange	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Aqueous–gas exchange	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Kinetic mineral precipitation–dissolution	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Mineral nucleation	Yes	Yes	Yes	Yes	No	Yes	No	No	No	Yes	No	No
Mineral solid-solutions	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	No	No
Equilibrium isotope fractionation	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	No	No
Kinetic isotope fractionation	Yes	Yes	Yes	No	No	Yes	Yes	No	Yes	Yes	Yes[c]	No
Aqueous kinetics	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Radioactive decay chains	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Microbial												
Monod kinetics	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Thermodynamic	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Biomass growth	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

[a] Not available in OGS, but OGS has built-in interfaces to different geochemical and biogeochemical solvers (GEM, PHREEQC, ChemApp, BRNS) that can implement Pitzer activity model

[b] DDL denotes Diffuse Double Layer, non-edl denotes Non-Electrostatic model, and CC denotes Constant Capacitance

[c] Not available in MIN3P-THCm, but available in a customized version of MIN3P [227]

Table 3 A comparison of the key numerical capabilities of reactive transport modeling codes

Capabilities/features	PHREEQC	HP1	PHT3D	OpenGeoSys	HYTEC	ORCHESTRA	TOUGHREACT	eSTOMP	HYDRO-GEOCHEM	CrunchFlow	MIN3P	PFLOTRAN
Coupling												
Reaction-induced porosity–permeability	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Coupled heat of reaction	No	No	No	Yes	No	No	Yes	No	Yes	No	No	Yes
Coupled deformation/ compaction[a]	No	No	No	Yes	No	No	C-E	No	EGM	C-E	No[b]	Yes
Reaction consumption of phase (H_2O, CO_2)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes
Electrical double layer transport	Yes	No	No	No	No	Yes	No	No	Yes	Yes	No	No
Numerical Scheme												
Operator splitting	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes
Global implicit	No	No	No	No	No	No	No	No	No	Yes	Yes	Yes
High Peclet number transport	Yes	No	Yes	Yes (FCT)[c]	No	Yes	No	Yes	Yes	Yes	Yes	Yes
Spatial discretization[d]	MC	FEM	FVM, MMC	FEM	FVM	MC	FVM	FVM	FEM, MMC	FVM	FVM	FVM
Time discretization[e]	TW	TW	TW	BE	TW	FE/ RK	BE/CN	BE	TW,Mid	BE	BE	BE
Computational												
Parallelization	No	No	No[f]	Yes	Yes	Yes	Partial	Yes	No	No	Yes	Yes
Inverse estimation	Yes	With PEST[g]	With PEST[g]	With PEST[g]	No	No	Yes	No	No	With PEST[g]	With PEST[g]	With PEST[g]
Graphical user interface	Yes	Yes	Yes	Yes	No	Yes	No	No	No	No	No	No
Open source	Yes	No	No	Yes	No	No	No	No	Yes	No	No	Yes

[a] C-E denotes compaction-erosion, and EGM denotes Equilibrium Geo-Mechanics Model

[b] Simplified 1-D approach following Neuzil [214]

[c] FCT refers to linearized algebraic flux corrected transport

[d] MC denotes mixing cell, FEM denotes Finite Element Method, FVM denotes Finite Volume Method and MMC denotes Modified Method of Characteristic or backward particle tracking

[e] BE denotes Backwards Euler, TW denotes time weighted difference including forward difference, backward difference, and Crank-Nicolson (CN) Central Difference, Mid denotes Mid difference, and RK denotes Runge-Kutta

[f] An MPI-based parallel version of PHT3D has been developed and is in the testing phase [228]

[g] PEST denotes Parameter Estimation Software Toolkit [229]

of charge, essentially solving the Nernst–Planck equation given in Eq. 48. The porosity of a cell can be updated in multicomponent diffusion simulations to account for dissolution or precipitation of minerals. Colloids, which can react as surface-complexation units, can be transported, coagulated, and resuspended depending on system properties and solute composition. Diffusion of interlayer (exchangeable) cations and of solutes in the diffuse layer of surfaces can be simulated.

Nearly any set of geochemical parameters and physical properties can be output to tab-delimited files or graphed with a built-in plotting capability that can produce multiple real-time plots simultaneously. Input for PHREEQC can be defined and run with a specialized module for Notepad++, or with one of two graphical user interfaces (PhreeqcI and Phreeqc for Windows; the latter uses PHREEQC version 2.18).

The wide range of geochemical capabilities offered by PHREEQC, its open-source code, as well as continued support and development by the U.S. Geological Survey have made it attractive for many researchers to couple it as a geochemical module to existing flow and transport codes that exceed PHREEQC's native transport capabilities. Specifically for this purpose, PHREEQC has been encapsulated in the module IPhreeqc [64] to allow all PHREEQC functions to be called from C, C++, Fortran, or from scripting languages (IPhreeqcCOM), such as Excel macros, Python, or Matlab. Coupling is performed with a sequential noniterative approach (SNIA), i.e., the same method as used in PHREEQC to couple transport and reactions. Some of these couplings are used to simulate unsaturated zone processes such as HPx [65, 66], saturated zone environments such as PHAST [64, 67] and PHT3D [68], and many more that are beyond the scope of this overview. At the time of this writing (April, 2014), PHREEQC is in its version 3 release. When the coupling to PHREEQC is based on the earlier release (version 2), it is noted as PHREEQC-2 in the descriptions below. All PHREEQC-related programs can be found at wwwbrr.cr.usgs.gov/projects/GWC_coupled or hydrochemistry.eu/downl.html.

4.2 HPx (HP1, HP2, HP3)

HPx, an acronym for HYDRUS [69] and PHREEQC [60], is a versatile coupled reactive transport code for variably saturated flow conditions. Originally released as a one-dimensional flow and transport model about a decade ago [70, 71], it is now also available for multidimensional flow and transport problems [65, 66]. Additionally, HPx codes are fully integrated in the well-designed graphical user interfaces of the HYDRUS codes [51]. Combining the capabilities of the individual HYDRUS and PHREEQC codes, HPx can be used to simulate many different processes in variably saturated porous media: (1) transient water flow, (2) transport of multiple aqueous and gaseous components, (3) heat transport, and (4) a broad range of low-temperature biogeochemical reactions, including interactions of the liquid phase with minerals, gases, exchangers, and sorption surfaces, described using thermodynamic equilibrium, kinetic, or mixed equilibrium–kinetic formulations.

Variably saturated water flow is described using the Richards equation, with the possibility of considering either uniform or dual-porosity (i.e., with water exchange between mobile and immobile zones) water flow models [69]. As HPx is specifically developed for soil systems, it includes (1) several single- and dual-porosity models describing soil hydraulic properties, with an option to consider hysteresis; (2) specific boundary conditions (BCs), such as atmospheric BCs with time-variable precipitation, evaporation and transpiration rates, free drainage, seepage face, and drain BCs; (3) an option to describe macro and small scale variability using different material types and linear scaling factors, respectively; and (iv) a compensated root water and solute uptake model [72], linked to a static or dynamic root distribution. Heat transport is described using an advection–diffusion–dispersion type equation for variably saturated conditions. Also, solute transport is simulated using the advection–diffusion–dispersion equation, with options to consider uniform, mobile/immobile water, and dual-porosity transport models [69]. As in the case of water flow, some features are included specifically for soil systems, such as passive and active uptake (or exudation) of solutes by plant roots. Diffusion in the gas phase is accounted for by explicitly taking into account variable gas contents. For two- and three-dimensional systems, anisotropy in the hydraulic conductivity and dispersivity can be defined.

PHREEQC-2 is currently used as the geochemical solver within HPx, preserving most functionalities of PHREEQC-2 (described in Section 4.1). Within the HPx framework, the BASIC scripting tool can also be used for a number of advanced options. One can define passive and active root solute uptake, where uptake parameters can depend on solution composition. The BASIC scripting tool can also be used to define the links between geochemical state variables and physical transport parameters. Relations between geochemical state variables and physical parameters, such as porosity, saturated hydraulic conductivity, dispersivity, tortuosity of the aqueous and gaseous phase (in calculations of effective diffusion coefficients), heat capacity, heat conductivity, and heat dispersivity, are not predefined but are all adjustable by users. This means, for example, that porosity–permeability–diffusion updates are not restricted to the Kozeny–Carmen approach or Archie's law, but can consider more complex relations accounting for the multiscale nature of some types of porous media [73].

Coupling between the transport and geochemical solvers (HYDRUS and PHREEQC-2, respectively) is by a sequential non-iterative approach. Operator-splitting errors can be controlled using an appropriate spatial and temporal discretization [71]. The flow and transport equations are solved numerically using Galerkin-type linear finite element schemes. The fully implicit temporal scheme is used to solve the flow equation. The water content term is evaluated using the mass conservative method proposed by Celia et al. [74]. A Crank–Nicholson or an implicit temporal scheme is used to solve the transport equations. The available spatial weighting schemes include, in addition to the Galerkin scheme, an upstream weighting scheme and a scheme with artificial dispersion. Additional measures are taken to improve solution efficiency for transient problems, including automatic time step adjustment and adherence to preset ranges of the Courant and Peclet numbers. Nevertheless, numerical schemes in HPx are applicable only for relatively low Peclet numbers, which seems appropriate for most flow and transport problems in soil systems. Time steps are adapted to ensure convergence and stability when solving the transport and flow equations.

HPx codes have been used to model a range of different processes. The versatility of HP1 was for example demonstrated for long-term transient flow and transport of major cations and heavy metals in a soil profile involving cation exchange processes [75], long-term U-migration in a soil profile following inorganic P-fertilization [76], inverse optimization of cation exchange parameters during transient flow [77], fate and transport of mercury in soils [78–80], chemical degradation of cement-based materials and alterations of transport parameters using a microstructural approach [73, 81], and carbon fluxes in soil systems [82].

4.3 PHT3D

PHT3D is a three-dimensional multicomponent reactive transport code specifically designed for simulating flow and reactive transport processes in saturated porous media. PHT3D couples the multispecies transport simulator MT3DMS [83] with the geochemical reaction model PHREEQC-2 [60] via sequential operator-splitting. The coupling to MT3DMS provides several options of solution techniques for transport: (1) method of characteristics (MOC), (2) modified method of characteristics (MMOC), (3) hybrid method of characteristics (HMOC), (4) upstream finite difference method, and (5) third-order TVD scheme [84]. The solution technique should be selected by the user based on the nature of the system being modeled (such as presence of sharp concentration gradients, redox reactions) and the selected discretization.

Through the flexible, generic nature of PHREEQC-2, PHT3D can handle a broad range of equilibrium and kinetic reactive processes, including aqueous complexation, mineral precipitation/dissolution, multisite cation exchange, and surface complexation reactions. The PHT3D code also has the capability to simulate kinetically reacting immobile components. Typical reactive processes such as microbial activity, NAPL dissolution, and isotopic fractionation can also be simulated. The structure of PHT3D code is such that these and other processes can be included through a PHREEQC-2 database files without modification of the PHT3D source code.

PHT3D was developed in the 1990s and has been applied to diverse groundwater problems. In the original version, transport was calculated during a time step, an input file was written for PHREEQC for geochemical calculations, and these steps were repeated for subsequent time steps until finished [85]. A second version was released in 2010 that tightened this reaction-transport coupling in the code to reduce computation time. In this version, PHREEQC is used for storing the chemical data of the model, including the chemical activities and the composition of surface complexes from the previous time step. A review of the developments in PHT3D version 2 and its potential applications were summarized by Appelo and Rolle [86].

Previous modeling studies using PHT3D targeted natural and enhanced remediation of organic (e.g., BTEX, CHCs) and inorganic (e.g., metals) contaminants and the geochemical changes occurring during their degradation. Applications of PHT3D also included modeling the fate and transport of pesticides, reactive transport of arsenic and uranium, trace metal remediation by in situ reactive zones, temperature-dependent pyrite oxidation, and isotopic fractionation during natural attenuation of organic pollutants [84]. Recently, PHT3D has been used to model interactions of seasonal aquifer thermal energy storage and groundwater contamination plumes [87] and radially symmetric flow and solute transport around point sources and sinks [88]. Recent enhancements of the code include implementation of electrokinetic transport to deliver a remediation compound within heterogeneous and low-permeability sediments for in situ chemical oxidation [89]. Further information regarding installation, user documentation, and benchmark test problems can be found at http://www.pht3d.org/.

PHT3D has been integrated into the PMWIN pre- or postprocessing package so as to enhance its graphical user interface (GUI) and visualization capabilities. This PMWIN coupling provides users the flexibility to select from existing reaction packages/database files or develop and integrate newly developed packages [90]. Another GUI available to PHT3D users is Visual MODFLOW.

4.4 OpenGeoSys

OpenGeoSys (OGS) is a scientific open-source initiative for numerical simulation of thermo–hydro–mechanical/chemical processes in porous and fractured media. The basic concept is to provide a flexible numerical framework for solving coupled multifield problems. The OGS code is targeting primarily applications in environmental geoscience, e.g., in the fields of contaminant hydrology, water resources management, waste deposits, or geothermal systems, but it has also been applied to new topics in energy storage [91].

The software is written with an object-oriented finite element method concept, including a broad spectrum of interfaces for pre- and postprocessing [92]. The OGS developer environment provides an open platform that includes professional software-engineering tools such as platform-independent compiling and automated result testing tools. To ensure the quality of the code and facilitate communications among different developers, more than 150 benchmarks are recently validated before any changes in the source code are released. In addition, the OGS community has been active in several international benchmarking initiatives, including e.g. DEVOVALEX (with applications mainly in waste repositories, Rutqvist [93], CO2BENCH and Sim-SEQ (in CO_2 sequestration, [94, 95]). The book containing over 100 wellverified benchmarks has been published recently [96].

In OGS, heterogeneous or porous-fractured media can be handled by dual continua or discrete approaches, i.e., by coupling elements of different dimensions. OGS has a built-in random-walk particle tracking method for Euler-Lagrange simulations [97] and can simulate incompressible and compressible flow [98], density-dependent flow [99], unsaturated flow [100], two-phase flow [101, 102], and overland flow [103]. All flow model components are available for non-isothermal conditions and for deformable porous media. Equations of state (EoS) for several fluids (gases, supercritical fluids) are available to module temperature-driven dynamics [104]. Multicomponent mass transport and (equilibrium and nonequilibrium) heat transport [105] modules are part of OGS.

The OGS Tool-Box [106] promotes functionality extension through code coupling interfaces for example coupling external geochemical and biogeochemical simulation tools such as PHREEQC/IPhreeqc, GEMS, and BRNS, in addition to the underlying internal process couplings. This flexibility has made it possible for OGS to simulate geochemical processes such as ion exchange, mineral dissolution/precipitation, and equilibrium reactions in partly saturated bentonites (OGS#PHREEQC-2 [107]), formation of solid solutions and radionuclide retardation (OGS#GEMS [108]), and thermochemistry for technical energy storage [91], as well as microbiological reactions such as Michaelis–Menten degradation kinetics to estimating in situ degradation rates [109] and organic carbon degradation via multiple microbial degradation pathways, dispersive mixing controlled bio-reactive transport with different reaction kinetics (OGS#BRNS [110]).

The OpenGeoSys community has been in development since the mid-1980s and the numerical simulator has been continuously re-engineered through Fortran, C, and C++ implementations and in the meantime the code has been optimized for massively parallel machines, e.g., JUQUEEN. The OGS community also developed continuous workflows that include various interfaces for pre- and postprocessing. Additionally, visual data integration became an important tool for establishing and validating data driven models [111] since three-dimensional visualization facilities, such as the UFZ-VISLAB (Leipzig, Germany), can be used for comprehensive systems analysis, computational steering, and demonstration purposes for stakeholder and authorities. Detailed information regarding code, benchmarks, and community is available through: *opengeosys.org*

4.5 HYTEC

HYTEC is a reactive transport code that integrates a wide variety of features and options that have evolved, after more than a decade of development, to a widely used and versatile simulation tool [112]. Solution capabilities for biogeochemistry are provided by the code CHESS (http://chess.ensmp.fr). The model accounts for many commonly encountered processes, including interface reactions (surface complexation with electrostatic correction and cation exchange), precipitation and dissolution of solid phases (minerals and colloids), organic complexation, and redox and microbial reactions. All reactions can be modeled using a full equilibrium, a full kinetic, or a mixed equilibrium–kinetic approach. All reactions can be modeled using a full equilibrium, a full kinetic, or a mixed equilibrium–kinetic approach. Thermodynamic data are taken from international databases, e.g., EQ 3/6 [113].

The hydrodynamic module of HYTEC is adapted for hydrodynamic conditions commonly encountered in the laboratory or in the field. The code allows for dual porosity, saturated, unsaturated or two-phase flow, variable boundary conditions, sinks, and sources [114]. HYTEC searches for an accurate solution to the multicomponent transport problem using an iterative, sequential, so-called strong coupling scheme. Strong coupling permits variable hydrodynamic parameters as a function of the local chemistry [115]. For example, the porosity of a porous medium decreases after massive precipitation of newly formed mineral phases, which modifies the water flow paths and transport parameters, e.g., diffusion coefficients. HYTEC solves this interdependency accurately, which makes the tool particularly useful for, e.g., cement alteration at long timescales (e.g., waste storage and performance assessment).

HYTEC has been used at various scales from micrometer to kilometer and within various geosciences fields: i.e., cement degradation, cement/clay interaction, polluted soils, waste dumps, radioactive waste disposal (performance assessment, near- and far-field processes [116, 117]), geological storage of acid gases [118, 119], and copper and uranium in situ recovery processes. Other applications concern the evolution and degradation of (geo)materials such as ashes, concrete, and cements; the latter often being simulated by a typical CEM-I cement, but more sophisticated models for cements can be used including sorption on primary or secondary calcium silicate hydrate phases, carbonation, and sulfate attack on the material [120, 121]. The strong coupling approach as outlined above makes HYTEC particularly useful for the modeling of long-term leaching of solidified wastes [122–124].

Efforts to develop, test, and validate the HYTEC model largely exceed the scope of a single laboratory. The Reactive Transport Consortium (*Pôle Géochimie-Transport*, http://pgt.geosciences.ensmp.fr) provides a national research framework with the objective of creating a long-term framework for the development of reactive transport models, reference studies, and new application domains. Already operational for several years, the collaborative efforts within the PGT have made it possible to make considerable progress in the domain of reactive transport modeling. Recent improvements include new solid solution, gas, and isotope modules. HYTEC is now able to deal with complex gas mixtures and to model accurately their interactions with water–salt–rock systems, and this ability has been tested against laboratory batch experiments [125]. The new isotope module also allows for the management of complex radioactive decay chains and chemical isotopic fractionation within the core of the code, allowing strong coupling between chemical and transport modules.

4.6 ORCHESTRA

ORCHESTRA is a platform developed by Meeussen [126] for modeling equilibrium chemistry, with the option of including kinetics and/or transport processes. ORCHESTRA does not enforce a specific model, but is rather a generic toolbox that allows users to create their own models using an object representation, which is stored in an object database and is fully user-definable.

In ORCHESTRA, reactive transport processes are implemented by a mixing-cell concept. This implies that transport systems can be composed of (well-mixed) cells and connections between these cells. The cells contain the information on the local physical and chemical composition, while the connections between the cells contain the mass transport equations (diffusion, convection, etc.). Both the connections between the cells, but also the literal equations involved in mass transport, are defined in text input files. Thus, ORCHESTRA provides the flexibility to the users to adapt the model structure and equations.

Effectively, the mixing-cell concept results in a finite difference scheme. In ORCHESTRA, it is possible to choose a sequential iteration (SIA) approach (predictor corrector method) or a non-iterative approach (SNIA) solved with a fourth order Runge–Kutta method. With SNIA, the kinetic reactions are solved using the same time step as the transport processes.

ORCHESTRA is coded in Java, which results in an executable code that runs on different operating systems (e.g., Windows, Linux, Unix, Solaris, OSX). Java also contains standard language constructs for parallel programming, which facilitates parallelization and makes efficient use of multiprocessor hardware. In contrast with the IPhreeqc method for parallelization that uses domain decomposition with nodes/cells predefined for each processor, the ORCHESTRA approach uses a single node pool, from which nodes are taken by each available processor. The advantage of the IPhreeqc method is that it is more suitable for distribution work over different physical machines. The advantage of the ORCHESTRA method is better load balancing for systems with strongly varying calculation times per node.

In ORCHESTRA, it is possible to obtain real-time graphical output for any chemical/physical parameter (e.g., concentration or pH profiles) during a calculation.

Historically, ORCHESTRA was first developed at the Macaulay Institute in Aberdeen, UK. Earliest applications of the code targeted chromium remediation and release from chromite ore-processing residue [127, 128]. Model development and verification then shifted to Wageningen University and Research Center, the Netherlands. Here, ORCHESTRA was used to model interactions between humic and fulvic acids, ions, and mineral surfaces [129–131]. These studies led to the implementation of CD-MUSIC, NICA-Donnan, Donnan ion exchange, and Ligand and Charge Distribution (LCD) model in ORCHESTRA for multi-surface adsorption modeling of cations and anions on organic matter, clay, and Fe oxides and the determination/interpretation of model parameters. ORCHESTRA has also been coupled to BIOCHEM for evaluating chemical speciation and eco-toxicological impacts of heavy metal uptake by biota [132]. ORCHESTRA has capabilities to model both saturated and unsaturated zones and has been extensively applied to model data from leaching tests, landfill leachate, pilot studies as well as groundwater data. For example, it has been used to implement a simple rhizosphere model by simulating diffusion and solute uptake towards a single cylindrical root [133]. Since 2010, code development has continued at the Nuclear Research and Consultancy Group. Recent applications of the model include coupling of ORCHESTRA with LeachXS database to improve understanding and prediction of the long-term performance of cementitious barriers used in nuclear applications. This thermo–hydro–mechanical (THM) coupling has also been used to assess long-term release behavior of sulfidic mining wastes [134], carbonation-induced corrosion in high-level waste tanks [135], and uncertainty quantification of thermodynamic parameters [136]. More information on code development and example applications is available at http://www.macaulay.ac.uk/ORCHESTRA/.

4.7 TOUGHREACT

TOUGHREACT [137–139] was developed by introducing reactive geochemistry into the framework of TOUGH2 V2 [140, 141]. TOUGH2 is a general purpose multiphase flow simulator that relies on a suite of equation of state (EOS) modules to compute fluid phase partitioning, and flow/transport of various components (e.g., water, CO_2, salt, air, tracers, radionuclides) in liquid, gas, and nonaqueous phases. Fluid flow by advection is computed using the multiphase extension of Darcy's Law, and diffusive mass transport is considered in all phases. The flow of heat by conduction and convection is also computed, taking into account temperature effects from phase changes. The evolution of each phase, including appearance and disappearance, and the partitioning of components between the different phases, are computed dynamically for each model grid block assuming local thermodynamic equilibrium for given conditions of temperature, pressure, and composition. The mass and energy balance equations are solved implicitly by Newton–Raphson iterations. An unstructured finite-volume (integrated finite-difference) numerical approach is implemented for the flow/transport computations. This allows modeling of porous and/or fractured systems and other types of systems with zones of different component mobility, through the use of multiple interacting continua (MINC) [44, 142].

By building on TOUGH2, TOUGHREACT simulates non-isothermal, multicomponent reactive transport of aqueous and gaseous components in variably saturated media. Reactive transport is solved by an operator-splitting approach that can be either iterative or non-iterative. Reactive processes considered include aqueous and surface complexation, ion exchange, mineral precipitation/dissolution, and gas exsolution/dissolution. Reactions among aqueous species and between aqueous species and minerals proceed under equilibrium and/or kinetic constraints. Other reactions operate under local thermodynamic equilibrium. The precipitation and dissolution of minerals is optionally coupled to porosity, permeability, and capillary pressure using various correlations that feed back into the multiphase flow computations. Aqueous and gaseous components are transported via advection and/or diffusion, following the calculation of multiphase fluxes. The transport step is followed with a fully implicit solve of the combined kinetic and equilibrium geochemistry.

TOUGHREACT has been applied to simulate a wide range of subsurface hydrological and biogeochemical environments. Applications have included, for example, geothermal systems [143–145], nuclear waste repositories [146–149], geologic carbon sequestration [150–154], and environmental remediation [155–157]. The development of TOUGHREACT has been ongoing since the late 1990s. Version V2 [137] was used in the benchmarks described in this special issue. More recent developments of TOUGHREACT include the coupling of geomechanical effects [158] and hybrid MPI-OpenMP parallelization of the reactive transport routines.

4.8 eSTOMP

eSTOMP is the parallel processing version of the Subsurface Transport Over Multiple Phases (STOMP) simulator [159]. The eSTOMP simulator can address variably saturated subsurface flow, transport, and reactions in heterogeneous porous media on the most powerful computers. The scalability of the formulation has been demonstrated on up to 131,000 processor cores for large complex biogeochemical reaction networks in highly resolved physically and geochemically heterogeneous sediments driven by dynamic variably saturated flow conditions.

Transient or steady-state flow can be confined/unconfined and/or variably saturated. Spatially variable material properties include anisotropic permeability/hydraulic conductivity (which can be saturation-dependent); diffusive porosity, longitudinal and transverse dispersivity, saturation function parameters (van Genuchten, Brooks-Corey, tabular data; Mualem, Burdine, Haverkamp), tortuosity, specific storativity, and compressibility.

Transport algorithms address advection, anisotropic dispersion, and interphase partitioning. High Peclet number total variation diminishing (TVD) transport schemes minimize numerical dispersion.

Arbitrarily complex reaction and rate law forms can be addressed in the biogeochemical reaction solver, as well as standard equilibrium and kinetic reactions for aqueous complexation, surface complexation, ion exchange, precipitation–dissolution reactions, and aqueous–gas exchange. Microbially mediated reactions include species-specific biomass production and decay, Monod-type rate laws with biomass dependencies, and thermodynamic controls. The modular reaction design currently provides the user with a range of solver capabilities including Pitzer, Debye–Hückel, and Davies activity models through two reaction solvers, ECKEChem [160] and BIOGEOCHEM [161].

A unique feature of the eSTOMP simulation capability is the option to couple highly detailed, mechanistic, genome-scale metabolic *in silico* models into the reaction module. In the constraint-based flux balance approach, hundreds of intracellular and environmental exchange reactions fundamentally account for the cell-scale physiology controlling cell maintenance, biosynthesis, and respiration. Under a maximization principle (e.g., growth), influxes of nutrients, electron donors, and acceptors drive a system of reactions with associated fluxes that can be determined using linear programming solvers. In this formulation, the biologically mediated reaction stoichiometry and rates are a function of the metabolic status of the organism, providing a more accurate depiction of these processes.

The eSTOMP simulator solves the partial-differential equations that describe the conservation of mass or energy quantities by employing integrated-volume finite-difference discretization to the physical domain and backward Euler discretization to the time domain. An operator splitting solution method is used for flow, transport, and reactions, each of which employs implicit time-stepping schemes. The resulting equations are nonlinear coupled algebraic equations, which are solved using Newton–Raphson iteration. Flow and solute transport are solved using parallel iterative conjugate gradient techniques as implemented in the Portable Extensible Toolkit for Scientific Computation (PETSc) libraries [162]. Differential algebraic equation solver techniques are used for the standard biogeochemical reaction network and the IBM ILOG CPLEX optimization solver package is used for the constraint-based system of metabolic pathway reactions. Input is directed through semi-formatted text files and output is available through a variety of user-directed formats. The simulator recognizes a number of boundary condition types and allows their specification both internally and externally to the computational domain. Gridding options include structured Cartesian and boundary fitted.

The memory and computational requirements for simulating coupled variably saturated and multicomponent biogeochemical reactive transport in highly resolved three-dimensional porous media typically exceeds the capabilities of standard desktop computing. Accordingly, eSTOMP was designed for execution on the full range of parallel processing computer architectures. eSTOMP uses one-sided communication and a global shared memory programming paradigm from the Global Array Toolkit (GA) library [163] for scalability, performance, and extensibility on massively parallel processing computers. The approach is compatible with the more commonly used Message Passing Interface (MPI) that is used by the PETSc global implicit solver in eSTOMP [162]. The principal benefit to this approach is that simulations with highly resolved process and property detail can be performed on a massively parallel computer in hours instead of weeks on a desktop computer. These efficiencies enable comprehensive exploration of alternative conceptual process models, hypothesis testing, and uncertainty quantification that represent a much larger expenditure of computational effort than the final production runs.

The theoretical and numerical approaches applied in the simulator have been documented in published theory guides [159, 160]. The simulator has undergone a rigorous testing procedure (http://stomp.pnnl.gov/QA/stomp-w-r.stm) and is maintained under version control procedures that meet NQA-1-2000 software requirements, as well as the requirements specified under DOE Order 414.1C for Safety Software.

4.9 HYDROGEOCHEM

HYDROGEOCHEM has evolved from a reactive chemical transport model developed by Yeh and co-workers [164] into a generic model that couples thermal (T), hydrology (H), geomechanics (M), and chemical (C) (THMC) processes (HC) [165], (THC) [166, 167]; (THMC) [168, 169]). It includes many numerical options to enhance its robustness and efficiency. The latest version of HYDROGEOCHEM involves four fully coupled modules: fluid flow, thermal transport, reactive biogeochemical transport, and geomechanic displacement and deformation [168, 169].

The pressure-based multiphase flow equations of arbitrary L fluid phases are transformed into a set of a total-pressure equation and (L-1) equations governing the evolutions of (L-1) accumulated degree of saturations. This set of equations are explicitly coupled via the storage coefficients and diffusion coefficients of all primary variables in every equation [151], which make the system much less stiff for numerical approximations. The transport equations governing the evolution of M species are transformed into a set of M equations governing the transport of M reaction extents. This effectively decouples the transport of components and kinetic variables from those for the rates of equilibrium reactions. As a result, it facilitates the iterative approach between a much-reduced number of partial differential equations of component and kinetic-variable transport and nonlinear algebraic equations that implicitly define the rates of equilibrium reactions [168, 170, 171]. In the geomechanics module, the media are treated as consisting of nonlinear viscous-elastic materials. This consideration enables the model to deal with large deformation and prevents a complete recovery after the stresses are released, which is more realistic than an elastic material treatment.

Similar types of governing equations to those described in Section 3 were implemented in HYDROGEOCHEM up to version 2. However, a different approach has been taken in the later versions. This alleviates the necessity of writing reactions in the canonical form for many types of reactions. Starting with a reaction network of N reactions involving M species, each reaction can involve any number of species, one can write M species transport equations based on the principle of chemical kinetics [172]. Performing Gauss–Jordan reduction of the reaction network [173–175], one obtains a system of M transport equations for M reaction extents, each of which is a linear combination of the M species concentrations [170, 171]. A reaction extent is called a component when there is no reaction term appearing in its transport equation. A reaction extent is called a kinetic-variable when there is one and only one independent kinetic reaction appearing in its transport equation. Similarly a reaction extent is called an equilibrium variable when there is one and only one independent equilibrium reaction appearing in its transport equation. This approach effectively decouples the computation of all N reaction rates from the simulation of a much reduced set of transport equations of components and kinetic variables as stated in the previous paragraph. It also allows the flexibility of programming any type of reaction rates into the code.

HYDROGEOCHEM can include a wide range of biogeochemical reactions such as aqueous complexation, adsorption/desorption, ion-exchange, precipitation/dissolution, redox, acid-base reactions, and microbial-mediated reactions. Multi-adsorbing sites and/or multi-ion exchange sites options are available for sorption reactions. Twenty-nine types of kinetic rate equations and four types of equilibrium rate equations have been implemented in the latest version of HYDROGEOCHEM [176, 177]. Other types of users' defined kinetic reactions and equilibrium reactions (e.g., the hydration reaction which evolves the site rather than conserves it) can be accommodated. Four schemes are available for coupling hydrologic transport and biogeochemical reactions: (1) fully implicit iteration approach [178], (2) operator-splitting approach, (3) predictor–corrector approach, and (4) mixed predictor–corrector and operator-splitting approach [169]. To enable the model to deal with complex media geometry, unstructured finite element meshes are used. For two-dimensional problems, both triangular elements and quadrilateral elements or the mixture of two types of elements can be employed to approximate complicated global geometry as well as irregular media interfaces. For three-dimensional problems, tetrahedral, hexahedral, triangular prism elements, or the mixture of these three types of elements can be selected. To make the model robust and efficient, Galerkin finite element is the choice for numerical approximation of the governing equations in multiphase phase flow module. For scalar transport modules of thermal and reactive transport, the Galerkin finite element, Petrov–Galerkin finite element, and/or Lagrangian–Eulerian finite element methods can be used to approximate the governing equations. For the geomechanic module, the linear successive approximation algorithm [179] is employed to approximate the governing equation of displacement.

HYDROGEOCHEM has been applied to many problems for research investigations as well as for practical simulations of radioactive waste disposal and redox zone migration. For example, it was employed to assess the adequacy of Kd-based models [180], used to investigate the performance of waste trench designs [181], and applied to remediation of contaminated lands [182]. It was applied to a sandy site to assess the effect of redox zones on the migration of metals [183], adapted to investigate the multi-segment reactions in contaminated aquifers [184], and employed to assess the redox geochemistry at shallow groundwaters [185]. The design capacity of fully coupled THMC processes is demonstrated in Yeh et al. [170].

4.10 CrunchFlow

CrunchFlow is a software package for simulating reactive transport developed by Steefel and co-workers and applied since 1988 to a variety of problems in the earth and environmental sciences. CrunchFlow is based on a finite volume discretization of the governing coupled partial differential equations that link flow, solute transport, and multicomponent equilibrium and kinetic reactions in porous and/or fluid media. Two approaches for coupling reactions and transport are available at runtime, (1) a global implicit approach that solves transport and reactions simultaneously (up to two dimensional), and (2) a time or operator splitting approach based on SNIA (up to three dimensional). The global implicit approach is based on a backwards Euler time discretization, with a global solution of the coupled reactive transport equations using Newton's method. The global implicit approach in CrunchFlow is implemented with the direct substitution approach (DSA) (72). An individual Newton iteration is solved using iterative conjugate gradient techniques as implemented in the PETSc libraries [162]. The global implicit approach in CrunchFlow can be run at arbitrarily large Courant numbers since there is no associated operator-splitting error, although other forms of error may still occur. Currently, the global implicit approach uses upstream weighting to simulate advective transport. The operator splitting approach, in contrast, requires time steps that are everywhere less than or equal to the Courant (for advection) and von Neumann (for diffusion) criteria. Advective transport is solved with a third-order accurate TVD approach that minimizes numerical dispersion while maintaining monotonicity. The use of the FORTRAN 90 language allows for dynamic allocation of memory for arrays, making it possible to choose the reaction-transport coupling scheme at runtime. Fully saturated flow is coupled sequentially to the reactive transport calculations—partially saturated flow and transport (including a gas phase) can be included, but currently requires calculation of the flow and liquid saturation field with separate software. Feedbacks on transport (flow and diffusion) rates as a result of reaction-induced porosity and permeability changes can be considered as well.

Diffusion can be modeled with either Fick's law or with the Nernst–Planck equation (currently without accounting for gradients in activity coefficients), making it possible to include differing diffusion coefficients for charged species while maintaining electroneutrality (48). CrunchFlow can also simulate accumulation and transport of ions within a discrete electrical double layer (EDL), with dynamic balancing of the surface charge on the mineral and in the Stern layer calculated with a surface complexation model. Dynamic treatment of the EDL thickness as a function of ionic strength can be used to simulate the changes in bulk versus EDL porosity. The treatment is based on a Donnan equilibrium or mean electrostatic approach to the EDL [186]. In the absence of charged mineral surfaces, this option becomes a more conventional dual porosity treatment of transport. Gas phase diffusion is handled by explicitly accounting for the composition of the gas phase and associated gradients.

The CrunchFlow software makes use of the canonical approach to reaction networks in which a set of equilibrium secondary or non-component aqueous complexes are defined in terms of primary or basis species that constitute the actual unknowns in the system, thus reducing substantially the number of governing equations and unknowns that need to be solved for once the secondary species are eliminated algebraically. Aqueous complexes can also be treated as kinetically controlled, in which case they are retained as primary species, while mineral reactions are treated in every case as kinetically controlled, although local equilibrium behavior can be simulated by choosing suitably large reaction rate constants. Multisite surface complexation reactions, with or without a formal treatment of electrostatic corrections, multisite ion exchange reactions (including Gaines–Thomas, Vanselow, and Gapon conventions), and gas–aqueous phase reactions are currently treated as equilibrium processes. Using an automatic read of a thermodynamic and kinetic database, the code can be used for reactive transport problems of arbitrary complexity and size (i.e., there is no a priori restriction on the number of species or reactions considered). Microbially mediated processes using classical Monod and inhibition terms, with or without an explicit thermodynamic term [26], can be simulated with a treatment of dynamic microbial populations.

The first use of predecessors of CrunchFlow was in simulations that took into account nucleation, precursors, Ostwald ripening, and crystal growth [187]. Steefel and Lasaga [188] made use of an early version of CrunchFlow to investigate non-isothermal, multidimensional numerical reactive transport model for hydrothermal systems, with kinetic treatment of mineral–water reactions. In a series of papers, Steefel and Lichtner [189–191] investigated diffusion-controlled reactive transport bordering active fractures, with consideration of porosity and reactivity feedbacks as a result of geochemical reactions. Making use of new capabilities for modeling the Nernst–Planck equation (electrochemical migration), Giambalvo et al. [192] investigated elemental fluxes from an off-axis hydrothermal system. Multisite, multicomponent simulation of ion exchange processes affecting the transport of ^{137}Cs below leaking tanks at the Hanford contaminated site was presented [22]. CrunchFlow was used as the basis of a diffusion and reaction + sediment burial model to explore uranium isotopic exchange and alpha recoil effects and included a rigorous treatment of steady-state burial and compaction [193]. In 2008, CrunchFlow was applied to reactive transport within a single pore, with a discussion of scale effects on geochemical reaction rates [1]. In Maher et al. [194], CrunchFlow was also used in a reactive transport analysis of weathering rates in the Santa Cruz chronosequence where it was shown that laboratory and field rates could be reconciled when nonlinear reaction kinetics were included. Navarre-Sitchler et al. [195] used CrunchFlow to simulate weathering rind formation based on the diffusion threshold model published earlier [196], which made use of CrunchFlow for three-dimensional diffusion simulations of the microtomography resolved pore network. A series of studies making use of the CrunchFlow software focused on microbially mediated biogeochemical reactions (Fe(III), U(VI), and sulfate reduction) associated with biostimulation at the Old Rifle site [197–201]. More recently, the capability for modeling of kinetic and equilibrium isotopic equilibration was added to the code. More information on the code can be found at http://www.csteefel.com/CrunchFlowIntroduction.html.

4.11 MIN3P

MIN3P is a multicomponent reactive transport code, specifically designed for simulating flow and reactive transport processes in variably saturated media. Unsaturated/saturated subsurface flows are described by Richards equation and the code uses the global implicit approach implemented using the direct substitution approach (DSA) for solution of the multicomponent advection–dispersion equation and biogeochemical reactions (72). Spatial discretization is performed based on the finite volume method, facilitating simulations in one, two, and three spatial dimensions. Advective transport terms can be described by upstream weighting, centered spatial weighting, or using a flux limiter technique to minimize numerical dispersion. Implicit time weighting is employed, which allows to use large time steps for problems that are strongly affected by water–rock interaction, without loss of accuracy. The highly nonlinear and coupled reactive transport equations are linearized using Newton's method.

The original MIN3P code developed by Mayer and co-workers [202] includes a generalized framework for kinetically controlled reactions, which can be specified through a database along with equilibrium processes. The general kinetic formulation includes intra-aqueous and dissolution–precipitation reactions in addition to geochemical equilibrium expressions for hydrolysis, aqueous complexation, oxidation–reduction, ion exchange, surface complexation, and gas dissolution–exsolution reactions. The generalized approach allows consideration of fractional order terms with respect to any dissolved species and mineral phases, which facilitates the incorporation of a variety of experimentally derived rate expressions. Monod and inhibition terms can be used to describe microbially mediated reactions. Dissolution–precipitation reactions can be described as surface-controlled or transport-controlled. The formulation also facilitates the consideration of any number of parallel reaction pathways, and reactions can be treated as irreversible or reversible processes.

Several code developments have been performed over the past decade to further improve the capabilities of MIN3P. Specifically, MIN3P has been enhanced to include a dual porosity formulation (MIN3P-DUAL [203]), allowing for reactive transport simulations involving mobile and immobile regions. This code was used in the assessment of the fate and transport of MTBE in a Chalk aquifer [204]. To describe gas entrapment and release due to water table fluctuations, as well as formation and migration of a discontinuous gas phase, the MIN3P-BUBBLE model was developed [205, 206]. Simulations conducted with this version of the code were related to problems involving in situ gas production or consumption at hydrocarbon spill sites under natural attenuation conditions. Investigations focused on oxygen and carbon transfer across the capillary fringe and the effect of these processes on contaminant degradation and groundwater plume migration. In addition, MIN3P was extended by implementing the dusty gas model (DGM), which describes multicomponent gas transport by advection and diffusion in the vadose zone (MIN3P-DUSTY, [36]). The code was used to simulate gas attenuation in landfill cover soils [207], methane production and oxidation in aquifers contaminated by organic compounds (e.g. an oil spill site), and sulfide oxidation in mine tailings [36, 208]. MIN3P was also enhanced by implementing the density coupling between flow and reactive transport (MIN3P-DENS, [209]) and was used to simulate permanganate-based remediation of chlorinated solvents under free convection conditions.

Recently, MIN3P-DENS was designated as the basis for all future MIN3P developments. A thermo–hydro–chemical (THC) formulation that extends the applicability of the code to reactive transport problems involving brines was implemented. The revised code (MIN3P-THCm) also accounts for the hydro-mechanical effects caused by surface loading [210]. Specifically, code enhancements included the implementation of the Harvie–Moller–Weare (HMW) model [211] based on Pitzer's equations [212]; fluid density calculations based on Pitzer's equations [213]; a simplified hydro-mechanical coupling formulation to account for the vertical compaction of the porous medium as presented by Neuzil [214]; and the energy balance in the porous medium. The MIN3P-THCm code was further enhanced by including water vapor transport and atmospheric boundary conditions [215]. The resulting code was used to illustrate the long-term stability of a sedimentary basin during a glaciation/deglaciation cycle [210] and to simulate carbon sequestration in ultramafic mine tailings [215]. MIN3P-THCm is the code used to contribute to the solution of the benchmarks presented in this special issue, unless otherwise noted.

In addition to the capabilities outlined above, MIN3PTHCm includes an option to account for permeability and tortuosity changes as a function of porosity modifications due to mineral dissolution–precipitation reactions. Current work involves the implementation of multicomponent diffusion and electrochemical migration based on the Nernst–Planck equation, and the parallelization of the code for both shared and distributed memory platforms.

Many applications of the MIN3P code family have utilized the capabilities to effectively simulate gas transport in the unsaturated zone, coupled with reactive solute transport.

For example, the code has been used by a number of researchers to simulate the generation and attenuation of acid rock drainage in mine waste (e.g., [202]), source zone natural attenuation of hydrocarbon spills in variably saturated media (e.g., [208, 216]), land application of food-processing waste water [217], and biogeochemical cycling of silicon in forest soils [218].

The MIN3P-THCm code is maintained under full-version control and is verified after each revision for a large suite of verification examples. More information on the code can be found at http://www.eos.ubc.ca/research/hydro/research/min3p/reactive_tran_web.htm.

4.12 PFLOTRAN

PFLOTRAN is an open-source, massively parallel multiscale and multiphysics code for subsurface flow and transport applications by Lichtner and co-workers [219]. A system of nonlinear partial differential equations describing non-isothermal multiphase flow, biogeochemical transport and geomechanics in porous media are solved. The code is designed to run on machines ranging from laptops and workstations to petascale leadership class computing architectures. Parallelization is achieved through domain decomposition using the Portable Extensible Toolkit for Scientific Computation (PETSc) libraries for its parallel framework [162]. PFLOTRAN has been developed from the ground up for parallel scalability and has been run on up to 2^{18} processor cores with problem sizes of over 2 billion degrees of freedom.

The code is written in object-oriented Fortran 2003. The subsurface flow processes available in PFLOTRAN include single-phase variably saturated flow (Richards equation), non-isothermal two-phase water-supercritical CO2 and air-water systems, thermal–hydrologic coupled heat and mass conservation, and three-phase ice–liquid–vapor (water) flow. The flow modes can be coupled to multicomponent reactive transport equations using either a fully implicit Newto–Raphson algorithm or operator splitting. The multicomponent reactive transport processes include aqueous complexation, sorption (isotherm-based, ion exchange, surface complexation), mineral precipitation/dissolution, and microbially mediated biodegradation. In addition, the mean age of a tracer and water can be calculated using Good's formulation [220]. All the processes can be solved on either structured or unstructured grids. To model non-isothermal flow and transport in fractured porous media, either a discrete fracture network approach can be used, or a multiple interacting continua formulation. A computationally efficient algorithm is used to rigorously decouple primary and secondary continuum equations for the multiple interacting continua method. Additional processes that can be solved include surface flow (under development) and geomechanics for elastic deformations. The surface flow mode can be coupled to the subsurface Richards mode, while the geomechanics mode can be sequentially coupled to any of the subsurface flow modes.

Subsurface and surface flow equations are discretized using the finite volume method while the geomechanics mode uses the finite element method. A novel feature of the code is its ability to run multiple input files and multiple realizations with heterogeneous permeability and porosity fields simultaneously on one or more processor cores per run. This feature is especially powerful when conducting sensitivity analyses and quantifying model uncertainties enabling computation of hundreds of realizations in the amount of time needed for a single realization. Since I/O is the bottleneck for large simulations especially with multiple realizations, PFLOTRAN uses the HDF5 API to read and write data in parallel. Obtaining better performance using parallel I/O is currently an active area of investigation.

PFLOTRAN is a multiple DOE laboratory effort with core developers from LANL, SNL, LBNL, and ORNL. PFLOTRAN is currently being used for several subsurface applications related to energy, climate, and national security. Some of these include nuclear waste disposal, CO_2 sequestration, enhanced geothermal systems, groundwater contamination, multiscale processes, and Arctic hydrology [221–225]. PFLOTRAN is released under GNU Lesser General Public License. PFLOTRAN has users from all over the world including research laboratories, industries, and universities. A regression suite of test problems is run nightly and with each new push of changes to the bitbucket repository for QA purposes. Information regarding installation and user documentation can be found at http://www.pflotran.org/, and can be freely downloaded from https://bitbucket.org/pflotran/pflotran-dev.

5 Summary and path forward

Hopefully it is clear from the foregoing discussion that subsurface reactive transport simulators have evolved dramatically in the last 10–15 years. It is now possible to simulate a wide range of complex, coupled subsurface processes with a number of different simulators, and with comparable results as demonstrated by the benchmark problems described in this volume. A range of coupling options have emerged as different groups have sought modularity of processes and applications in some cases, tightly coupled solution procedures in others. In essentially every case, there are tradeoffs between the various approaches and the choice of one or the other should likely depend on the specific subsurface environmental problem that needs to be solved.

We would argue, therefore, that the progress to date has been impressive, to the point where reactive transport modeling might even be recognized in the future as a distinct discipline within the earth and environmental sciences, rather than a mongrel activity wedged between hydrology and geochemistry. Nonetheless, there is much that remains to be done in this field. Solid solutions need to be incorporated into reactive transport models in a more extensive manner than achieved in current implementations. Coupling of hydrology and geochemistry with mechanics, for example, is still in the initial stages of development. More sophisticated (and inevitably complex) treatments of microbial community function that are coupled to environmental conditions are also possible in the future. Treatments of multiscale phenomena are only now beginning to be explored, in most cases through multiple continuum approaches. This topic is likely to be a primary focus in the future [222, 226]. Eventually, one expects to have subsurface environmental simulators that couple to surface water and take more fully into account the interactions with plants and the atmosphere. In this regard, links to landforms are likely to become important.

References

1. Li, L., Steefel, C.I., Yang, L.: Scale dependence of mineral dissolution rates within single pores and fractures. Geochim. Cosmochim. Acta. **72**, 360–377 (2008)
2. Molins, S., Trebotich, D., Steefel, C.I., Shen, C.: An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation. Water Resour. Res. **48**, W03527 (2012)
3. Steefel, C.I., Molins, S., Trebotich, D.: Pore scale processes associated with subsurface CO_2 injection and sequestration. Rev. Mineral. Geochem. **77**, 259–303 (2013)
4. Oostrom, M., Mehmani, Y., Romero-Gomez, P., Tang, Y., Liu, H., Yoon, H., Zhang, C.: Pore-scale and continuum simulations of solute transport micromodel benchmark experiments. Comput. Geosci., 1–23 (2014)
5. Aris, R.: Prolegomena to the rational analysis of systems of chemical reactions. Arch. Ration. Mech. Anal. **19**, 81–99 (1965)
6. Bowen, R.M.: On the stoichiometry of chemically reacting materials. Arch. Ration. Mech. Anal. **29**, 114–124 (1968)
7. Hooyman, G.J.: On thermodynamic coupling of chemical reactions. Proc. Natl. Acad. Sci. **47**, 1169–1173 (1961)
8. Kirkner, D.J., Reeves, H.: Multicomponent mass transport with homogeneous and heterogeneous chemical reactions: Effect of chemistry on the choice of numerical algorithm I. Theory. Water Resour. Res. **24**, 1719–1729 (1988)
9. Lichtner, P.C.: Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. Geochim. Cosmochim. Acta **49**, 779–800 (1985)
10. Reed, M.H.: Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases, and an aqueous phase. Geochim. Cosmochim. Acta **46**, 513–528 (1982)
11. Van Zeggeren, F., Storey, S.H.: The computation of chemical equilibria, p. 176. Cambridge University Press, Cambridge (1970)
12. Steefel, C.I., Lasaga, A.C.: A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. Am. J. Sci. **294**, 529–592 (1994)
13. Davis, J.A., Meece, D.E., Kohler, M., Curtis, G.P.: Approaches to surface complexation modeling of uranium (VI) adsorption on aquifer sediments. Geochim. Cosmochim. Acta **68**, 3621–3641 (2004)
14. Kulik, D.A.: Thermodynamic concepts in modeling sorption at the mineral-water interface. Rev. Mineral. Geochem. **70**, 125–180 (2009)
15. Dzombak, D.A., Morel, F.M.M.: Surface complexation modeling: hydrous ferric oxide, p. 393. Wiley, New York (1990)
16. Wang, Z., Giammar, D.E.: Mass action expressions for bidentate adsorption in surface complexation modeling: Theory and practice. Environ. Sci. Technol. **47**, 3982–3996 (2013)
17. Davis, J.A., Coston, J.A., Kent, D.B., Fuller, C.C.: Application of the surface complexation concept to complex mineral assemblages. Environ. Sci. Technol. **32**(19), 2820–2828 (1998)
18. Liu, C., Zachara, J.M., Qafoku, N.P., Wang, Z.: Scale-dependent desorption of uranium from contaminated subsurface sediments. Water Resour. Res. **8**, 44 (2008)
19. Vanselow, A.P.: Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. Soil Sci. **33**, 95–114 (1932)
20. Sposito, G.: The thermodynamics of soil solutions, p. 223. Oxford University Press, Oxford (1981)
21. Appelo, C.A.J., Postma, D.: Geochemistry, groundwater, and pollution. A.A. Balkema, Rotterdam, p 649 (1993)
22. Steefel, C.I., Carroll, S., Zhao, P., Roberts, S.: Cesium migration in Hanford sediment: A multi-site cation exchange model based on laboratory transport experiments. J. Contam. Hydrol. **67**, 219–246 (2003)
23. Aagaard, P., Helgeson, H.C.: Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions; I, Theoretical considerations. Am. J. Sci. **282**(3), 237–285 (1982)
24. Lasaga, A.C.: Chemical kinetics of water-rock interactions. J. Geophys. Res. Solid Earth (1978–2012) **89**(B6), 4009–4025 (1984)
25. Rittmann, B.E., McCarty, P.L.: Environmental biotechnology. McGraw Hill, New York (2001)
26. Jin, Q., Bethke, C.M.: Predicting the rate of microbial respiration in geochemical environments. Geochim. Cosmochim. Acta **69**, 1133–1143 (2005)
27. Bear, J.: Dynamics of fluids in porous media, p. 764. Dover Publications (1972)
28. Steefel, C.I., Maher, K.: Fluid-rock interaction: A reactive transport approach. Rev. Mineral. Geochem. **70**, 485–532 (2009)
29. Neuman, S.P.: Saturated-unsaturated seepage by finite elements. J. Hydrol. Div. Am. Soc. Civ. Eng. **99**(HY12), 2233–2250 (1973)
30. Panday, S., Huyakorn, P.S., Therrien, R., Nichols, R.L.: Improved three-dimensional finite-element techniques for field simulation of variably-saturated flow and transport. J. Contam. Hydrol. **12**, 3–33 (1993)
31. Van Genuchten, M.T.: A closed form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Sci. Soc. Am. J. **44**, 892–898 (1980)
32. Brooks, R.H., Corey, A.T.: Hydraulic properties of porous media. Colorado State Univ., Hydrology Paper No. 3, p. 27 (1964)
33. Luckner, L., Van Genuchten, M.T., Nielsen, D.R.: A consistent set of parametric models for the two-phase flow of immiscible

fluids in the subsurface. Water Resour. Res. **25**(10), 2187–2193 (1989)
34. Millington, R.J.: Gas diffusion in porous media. Science **130**(3367), 100–102 (1959)
35. Mayer, K.U., Blowes, D.W., Frind, E.O.: Reactive transport modeling for the treatment of an in situ reactive barrier for the treatment of hexavalent chromium and trichloroethylene in groundwater. Water Resour. Res. **37**, 3091–3103 (2001)
36. Molins, S., Mayer, K.U.: Coupling between geochemical reactions and multicomponent gas diffusion and advection – a reactive transport modeling study. Water Resour. Res. **43**, W05435 (2007)
37. Cheadle, M.J., Elliott, M.T., McKenzie, D.: Percolation threshold and permeability of crystallizing igneous rocks: The importance of textural equilibrium. Geology **32**, 757–760 (2004)
38. Verma, A., Pruess, K.: Thermohydrological conditions and silica redistribution near high-level nuclear wastes emplaced in saturated geological formations. J. Geophys. Res. Solid Earth **93**(B2), 1159–1173 (1988)
39. Vaughan, P.J.: Analysis of permeability reduction during flow of heated aqueous fluid through Westerly Granite. In: Tsang, C.-F. (ed.) Coupled processes associated with nuclear waste repositories. Academic Press, New York (1989)
40. Slider, H.C.: Practical petroleum reservoir engineering methods, An Energy Conservation Science. Petroleum Publishing Company, Tulsa (1976)
41. Wu, Y.S.: On the effective continuum method for modeling multiphase flow, multicomponent transport, and heat transfer in fractured rock. In: Faybishenk, B., Witherspoon, P.A., Benson, S.M. (eds.) Dynamics of Fluids Fractured Rock, pp. 299–312 (2000)
42. Barenblatt, G.I., Zheltov, I.P., Kochina, I.N.: Basic concepts in the theory of seepage of homogeneous liquids in fissured rocks [strata]. J. Appl. Math. Mech. **24**, 1286–1303 (1960)
43. Warren, J.E., Root, P.J.: The behavior of naturally fractured reservoirs. SPE J. **3**, 245–255 (1963)
44. Pruess, K., Narasimhan, T.N.: A practical method for modeling fluid and heat flow in fractured porous media. Soc. Pet. Eng. J. **25**, 14–26 (1985)
45. Snow, D.T.: A parallel plate model of fractured permeable media, Ph.D. dissertation, p. 331. University of California, Berkeley (1965)
46. Arora, B., Mohanty, B.P., McGuire, J.T.: Inverse estimation of parameters for multidomain flow models in soil columns with different macropore densities. Water Resour. Res. **47**, 1–17 (2011)
47. Wu, Y.S., Di, Y., Kang, Z., Fakcharoenphol, P.: A multiple-continuum model for simulating single-phase and multiphase flow in naturally fractured vuggy reservoirs. J. Pet. Sci. Eng. **78**, 13–22 (2011)
48. Aradóttir, E.S.P., Sigfússon, B., Sonnenthal, E.L., Björnsson, G., Jónsson, H.: Dynamics of basaltic glass dissolution–capturing microscopic effects in continuum scale models. Geochim. Cosmochim. Acta **121**, 311–327 (2013)
49. Lichtner, P.C.: Critique of dual continuum formulations of multicomponent reactive transport in fractured porous media. In: Faybishenk, B., Witherspoon, P.A., Benson, S.M. (eds.) Dynamics of Fluids Fractured Rock, pp. 281–298 (2000)
50. Berkowitz, B.: Characterizing flow and transport in fractured geological media: A review. Adv. Water Resour. **25**, 861–884 (2002)
51. Šimůnek, J., Jarvis, N.J., Van Genuchten, M.T., Gärdenäs, A.: Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. J. Hydrol. **272**, 14–35 (2003)
52. MacQuarrie, K.T., Mayer, K.U.: Reactive transport modeling in fractured rock: A state-of-the-science review. Earth Sci. Rev. **72**, 189–227 (2005)
53. Somerton, W.H., El-Shaarani, A.H., Mobarak, S.M.: High temperature behavior of rocks associated with geothermal type reservoirs. In: SPE California Regional Meeting. Society of Petroleum Engineers (1974)
54. Steefel, C.I., MacQuarrie, K.T.B.: Approaches to modeling reactive transport in porous media. In: Lichtner, P.C., Steefel, C.I., Oelkers, E.H. (eds.) Reactive Transport in Porous Media, vol. 34, pp. 83–125. Reviews in Mineralogy (1996)
55. Kulik, D.A., Wagner, T., Dmytrieva, S.V., Kosakowski, G., Hingerl, F.F., Chudnenko, K.V., Berner, U.R.: GEM-Selektor geochemical modeling package: Revised algorithm and GEMS3K numerical kernel for coupled simulation codes. Comput. Geosci. **17**(1), 1–24 (2013)
56. Leal, A.M.M., Blunt, M.J., LaForce, T.C.: Efficient chemical equilibrium calculations for geochemical speciation and reactive transport modelling. Geochim. Cosmochim. **131**, 301–322 (2014)
57. Saaltink, M.W., Carrera, J., Ayora, C.: On the behavior of approaches to simulate reactive transport. J. Contam. Hydrol. **48**, 213–235 (2001)
58. Calderhead, A., Mayer, K.U.: Comparison of the suitability of the global implicit method and the sequential non-iterative approach for multicomponent reactive transport modelling. In: Proceedings of 5th Joint IAH-CNC/CGS Conference, Québec City, Québec, Canada, pp. 24–28 (2004)
59. Lichtner, P.C.: Time-space continuum description of fluid/rock interaction in permeable media. Water Resour. Res. **28**, 3135–3155 (1992)
60. Parkhurst, D.L., Appelo, C.A.J.: User's guide to PHREEQ C (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations, Water-Resources Investigations, Report 99–4259, Denver, Co, USA, p. 312 (1999)
61. Parkhurst, D.L., Appelo, C.A.J.: Description of input and examples for PHREEQC version 3—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43 (2013)
62. Appelo, C.A.J., Parkhurst, D.L., Post, V.E.A.: Equations for calculating hydrogeochemical reactions of minerals and gases such as CO_2 at high pressures and temperatures. Geochim. Cosmochim. Acta **125**, 49–67 (2014)
63. Thorstenson, D.C., Parkhurst, D.L.: Calculation of individual isotope equilibrium constants for geochemical reactions. Geochim. Cosmochim. Acta **11**(68), 2449–2465 (2004)
64. Charlton, S.R., Parkhurst, D.L.: Phast4Windows: A 3D graphical user interface for the reactive-transport simulator PHAST. Groundwater **4**(51), 623–628 (2013)
65. Šimůnek, J., Jacques, D., Šejna, M., van Genuchten, M.T.: The HP2 Program for HYDRUS (2D/3D): A coupled code for simulating two-dimensional variably-saturated water flow, heat transport, and biogeochemistry in porous media, Version 1.0, PC Progress, Prague, Czech Republic, p. 76 (2012)
66. Šimůnek, J., Jacques, D., Langergraber, G., Bradford, S.A., Šejna, M., van Genuchten, M.T.: Numerical modeling of contaminant transport using HYDRUS and its specialized modules, vol. 93, pp. 265–284 (2013). ISSN: 0970-4140 Coden-JIISAD
67. Parkhurst, D.L., Kipp, K.L., Charlton, S.R.: PHAST Version 2—a program for simulating groundwater flow, solute transport, and

multicomponent geochemical reactions: U.S. Geological Survey Techniques and Methods 6–A35, p. 235 (2010)

68. Prommer, H., Post, V.E.A.: PHT3D, A Reactive Multicomponent Transport Model for Saturated Porous Media. User's Manual v2.10 (2010). http://www.pht3d.org
69. Šiůnek, J., van Genuchten, M.T.: Modeling non-equilibrium flow and transport processes using HYDRUS. Vadose Zone J. **7**(2), 782–797 (2008)
70. Jacques, D., Šimůnek, J.: User Manual of the Multicomponent Variably-Saturated Flow and Transport Model HP1, Description, Verification and Examples, Version 1.0, SCK•CEN-BLG-998, Waste and Disposal, SCK•CEN, Mol, Belgium, p. 79 (2005)
71. Jacques, D., Šimůnek, J., Mallants, D., van Genuchten, M.T.: Operator-splitting errors in coupled reactive transport codes for transient variably saturated flow and contaminant transport in layered soil profiles. J. Contam. Hydrol. **88**, 197–218 (2006)
72. Šimůnek, J., Hopmans, J.W.: Modeling compensated root water and nutrient uptake. Ecological Modeling **220**, 505–521 (2009)
73. Jacques, D., Šimůnek, J., Mallants, D., van Genuchten, M.T., Yu, L.: A coupled reactive transport model for contaminant leaching from cementitious waste matrices accounting for solid phase alterations. In: Proceedings Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium (2011)
74. Celia, M.A., Bououtas, E.T., Zarba, R.L.: A general mass-conservative numerical solution for the unsaturated flow equation. Water Resour. Res. **26**, 1483–1496 (1990)
75. Jacques, D., Šimůnek, J., Mallants, D., van Genuchten, M.T.: Modelling coupled water flow, solute transport and geochemical reactions affection heavy metal migration in a Podzol soil. Geoderma **145**, 449–461 (2008)
76. Jacques, D., Šimůnek, J., Mallants, D., van Genuchten, M.T.: Modeling coupled hydrogeologic and chemical processes: Long-term uranium transport following phosphorus fertilization. Vadose Zone J. **7**(2), 698–711 (2008)
77. Jacques, D., Smith, C., Šimůnek, J., Smiles, D.: Inverse optimization of hydraulic, solute transport, and cation exchange parameters using HP1 and UCODE to simulate cation exchange. J. Contam. Hydrol. **142–143**, 109–125 (2012)
78. Bessinger, B.A., Marks, C.D.: Treatment of mercury-contaminated soils with activated carbon: A laboratory, field, and modeling study. Remediation (The journal of Environmental Cleanup Costs, Technologies, & Techniques), **21**(1), 115–135 (2010). doi:10.1002/rem.20275
79. Leterme, B., Jacques, D.: Modelling of mercury fate and transport in soil systems. In: Proceedings of the 12th International UFZ-Deltares Conference on Groundwater-Soil-Systems and Water Resource Management - AQUACONSOIL 2013 (2013). www.aquaconsoil.org/AquaConSoil2013/Proceedings.html
80. Leterme, B., Blanc, P., Jacques, D.: A reactive transport model for mercury fate in soil – application to different anthropogenic pollution sources. Environmental Science and Pollution Research, (under review) (2014)
81. Jacques, D., Maes, N., Perko, J., Seetharam, S.C., Phung, Q.T., Patel, R., Soto, A., Liu, S., Wang, L., De Schutter, G., Ye, G., van Breugel, K.: Concrete in engineered barriers for radioactive waste disposal facilities - phenomenological study and assessment of long term performance. In: Proceedings of the ASME 2013 15th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM2013-96282 (2013)
82. Thaysen, E.M., Jacques, D., Jessen, S., Andersen, C.E., Laloy, E., Ambus, P., Postma, D., Jakobsen, I.: Controls on carbon dioxide fluxes across the unsaturated zone of cropped and unplanted soil mesocosms. Biogeosciences **11**, 4251–4299 (2014)
83. Zheng, C., Wang, P.P.: MT3DMS: A modular three-dimensional multispecies transport model for simulation of advection, dispersion and chemical reactions of contaminants in ground water systems: documentation and user's guide. Contract Report SERDP-99–1, U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi (available at http://hydro.geo.ua.edu/mt3d) (1999)
84. Prommer, H., Post, V.E.A.: PHT3D, A Reactive multicomponent transport model for saturated porous media. User's Manual v2.10 (2010). http://www.pht3d.org
85. Prommer, H., Barry, D.A., Zheng, C.: MODFLOW/MT3DMS-based reactive multicomponent transport modeling. Ground Water **41**, 247–257 (2003)
86. Appelo, C.A.J., Rolle, M.: PHT3D: A reactive multicomponent transport model for saturated porous media. Ground Water **5**(48), 627–632 (2010)
87. Zuurbier, K.G., Hartog, N., Valstar, J., Post, V.E.A., van Breukelen, B.M.: The impact of low-temperature seasonal aquifer thermal energy storage (SATES) systems on chlorinated solvent contaminated groundwater: modeling of spreading and degradation. J. Contam. Hydrol. **147**, 1–13 (2013)
88. Wallis, I., Prommer, H., Post, V.E.A., Vandenbohede, A., Simmons, C.T.: Simulating MODFLOW-based reactive transport under radially symmetric flow conditions. Groundwater **51**, 398–413 (2013)
89. Wu, M.Z., Reynolds, D.A., Prommer, H., Fourie, A., Thomas, D.G.: Numerical evaluation of voltage gradient constraints on electrokinetic injection of amendments. Adv. Water Resour. **38**, 60–69 (2012)
90. Chiang, W.H. 3D Groundwater modeling with PMWIN, 2nd ed., p. 397. Springer-Verlag, The Netherlands (2005)
91. Nagel, T., Shao, H., Singh, A.K., Watanabe, N., Roßkopf, C., Linder, M., Wörner, A., Kolditz, O.: Non-equilibrium thermochemical heat storage in porous media: Part 1 – conceptual model. Energy **60**, 254–270 (2013)
92. Kolditz, O., Bauer, S., Bilke, L., Böttcher, N., Delfs, J.O., Fischer, T., Görke, U.J., Kalbacher, T., Kosakowski, G., McDermott, C.I., Park, C.H., Radu, F., Rink, K., Shao, H., Shao, H.B., Sun, F., Sun, Y.Y., Singh, A.K., Taron, J., Walther, M., Wang, W., Watanabe, N., Wu, N., Xie, M., Xu, W., Zehner, B.: OpenGeoSys: An open-source initiative for numerical simulation of thermo-hydro-mechanical/chemical (THM/C) processes in porous media. Environ. Earth Sci. **67**, 589–599 (2012)
93. Rutqvist, J., Barr, D., Birkholzer, J.T., Chijimatsu, M., Kolditz, O., Liu, Q., Oda, Y., Wang, W., Zhang, C.: Results from an international simulation study on coupled thermal, hydrological, and mechanical processes near geological nuclear waste repositories. J. Nucl. Technol. **163**, 101–109 (2008)
94. Kolditz, O., Bauer, S., Beyer, C., Böttcher, N., Dietrich, P., Görke, U.-J., Kalbacher, T., Park, C.-H., Sauer, U., Schütze, C., Shao, H.B., Singh, A.K., Taron, J., Wang, W., Watanabe, N.: A systematic benchmarking approach for geologic CO_2 injection and storage. Environ. Earth Sci. **67**, 613–632 (2012)
95. Mukhopadhyay, S., Birkholzer, J.T., Nicot, J.P., Hosseini, S.A.: A single site multi-model comparative study for CO_2 injection field test: An introduction to Sim-SEQ. Environ. Earth Sci. **67**, 601–611 (2012)
96. Kolditz, O., Shao, H., Görke, U.-J., Wang, W. (eds.): Thermo-hydro-mechanical-chemical processes in fractured porous media. Lecture Notes in Computational Science and Engineering, vol. 86. Springer, Heidelberg (2012)

97. Park, C.-H., Beyer, C., Bauer, S., Kolditz, O.: A study of preferential flow in heterogeneous media using random walk particle tracking. Geosci. J. **12**, 285–297 (2008)
98. Gräbe, A., Rink, K., Fischer, T., Sun, F., Wang, W., Rödiger, T., Siebert, C., Kolditz, O.: Numerical analysis of the groundwater regime in the Western Dead Sea Escarpment. Environ. Earth Sci. **69**, 571–586 (2013)
99. Singh, A.K., Baumann, G., Henninges, J., Görke, U.-J., Kolditz, O.: Numerical analysis of thermal effects during carbon dioxide injection with enhanced gas recovery: A theoretical case study for the Altmark gas field. Environ. Earth Sci. **67**, 497–509 (2012)
100. Wang, W., Rutqvist, J., Gorke, U.-J., Birkholzer, J.T., Kolditz, O.: Non-isothermal flow in low permeable porous media: A comparison of unsaturated and two-phase flow approaches. Environ. Earth Sci. **62**, 1197–1207 (2011)
101. Kolditz, O., de Jonge, J.: Non-isothermal two-phase flow in porous media. Comput. Mech. **33**, 345–364 (2004)
102. Park, C.-H., Boettcher, N., Wang, W., Kolditz, O.: Are upwind techniques in multi-phase flow models necessary. J Comp. Phys. **230**, 8304–8312 (2011)
103. Delfs, J.-O., Park, C.-H., Kolditz, O.: A sensitivity analysis of Hortonian flow. Adv. Water Resour. **32**, 1386–1395 (2009)
104. Böttcher, N., Kolditz, O., Liedl, R.: Evaluation of equations of state for CO2 in numerical simulations. Environ. Earth Sci. **67**, 481–495 (2012)
105. Watanabe, N., McDermott, C., Wang, W., Taniguchi, T., Kolditz, O.: Uncertainty analysis of thermo-hydro-mechanical processes in heterogeneous porous media. Comput. Mech. **45**, 263–280 (2010)
106. Kalbacher, T., Delfs, J.O., Shao, H., Wang, W., Walther, M., Samaniego, L., Schneider, C., Musolff, A., Centler, F., Sun, F., Hildebrandt, A., Liedl, R., Borchardt, D., Krebs, P., Kolditz, O.: The IWAS-ToolBox: Software coupling for an integrated water resources management. Environ. Earth Sci. **65**, 1367–1380 (2012)
107. Xie, M., Bauer, S., Kolditz, O., Nowak, T., Shao, H.: Numerical simulation of reactive processes in an experiment with partially saturated bentonite. J Contam. Hydrol. **83**, 122–147 (2006)
108. Shao, H., Kolditz, O., Kulik, D.A., Pfingsten, W., Kosakowski, G.: Reactive transport of multiple non-ideal solid solutions. Appl. Geochem. **24**, 1287–1300 (2009)
109. Beyer, C., Bauer, S., Kolditz, O.: Uncertainty assessment of contaminant plume length estimates in heterogeneous aquifers. J. Contam. Hydrol. **87**, 73–95 (2006)
110. Centler, F., Shao, H., Park, C.-H., de Biase, C., Kolditz, O., Thullner, M.: GeoSysBRNS – a flexible multi-dimensional reactive transport model for simulating biogeochemical subsurface processes. Comput. Geosci. **36**, 397–405 (2010)
111. Rink, K., Kalbacher, T., Kolditz, O.: Visual data management for hydrological analysis. Environ. Earth Sci. **65**, 1395–1403 (2012)
112. van der Lee, J., De Windt, L., Lagneau, V., Goblet, P.: Module-oriented modeling of reactive transport with HYTEC. Comput. Geosci. **29**, 265–275 (2003)
113. Wolery, T.: EQ3/6. A software package for geochemical modelling of aqueous systems: Package overview and installation guide (version 7.0). Technical Report UCRL-MA-110662 PT I ed. Lawrence Livermore National Laboratory, USA (1992)
114. van der Lee, J., Lagneau, V.: Rigorous methods for reactive transport in unsaturated porous medium coupled with chemistry and variable porosity. In: Miller, C.T., Farthing, M.W., Gray, W.G., Pinder, G.F. (eds.) Computational Methods in Water Resources (CMWR XV), vol. 48, pp. 861–868. Elsevier (2004)
115. Lagneau, V., van der Lee, J.: Operator-splitting-based reactive transport models in strong feedback of porosity change: The contribution of analytical solutions for accuracy validation and estimator improvement. J. Contam. Hydrol. **112**, 118–129 (2010)
116. Debure, M., De Windt, L., Frugier, P., Gin, S.: HLW glass dissolution in the presence of magnesium carbonate: Diffusion cell experiment and coupled modeling of diffusion and geochemical interactions. J. Nucl. Mater. **443**, 507–521 (2013)
117. De Windt, L., Marsal, F., Corvisier, J., Pellegrini, D.: Modeling of oxygen gas diffusion and consumption during the oxic transient in a disposal cell of radioactive waste. Appl. Geochem. **41**, 115–127 (2014)
118. Lagneau, V., Pipart, A., Catalette, H.: Reactive transport modelling and long term behaviour of CO2 sequestration in saline aquifers. Oil Gas Sci. Technol. **60**, 231–247 (2005)
119. Jacquemet, N., Pironon, J., Lagneau, V., Saint-Marc, J.: Armouring of well cement in H_2S-CO_2 saturated brine by calcite coating – experiments and numerical modeling. Appl. Geochem. **27**, 782–795 (2012)
120. De Windt, L., Devillers, P.: Modeling the degradation of Portland cement pastes by biogenic organic acids. Cem. Concr. Res. **40**, 1165–1174 (2010)
121. De Windt, L., Deneele, D., Maubec, N.: Kinetics of lime/bentonite pozzolanic reactions at 20 and 50 °C: Batch tests and modeling. Cem. Concr. Res. **59**, 34–42 (2014)
122. Dabo, D., Badreddine, R., De Windt, L., Drouadaine, I.: Ten-year chemical evolution of leachate and municipal solid waste incineration bottom ash used in a test road site. J. Hazard. Mater. **172**, 904–913 (2007)
123. De Windt, L., Badreddine, R., Lagneau, V.: Long-term reactive transport modelling of stabilized/solidified waste: From dynamic leaching tests to disposal scenarios. J. Hazard. Mater. **139**, 529–536 (2007)
124. De Windt, L., Badreddine, R.: Modelling of long-term dynamic leaching tests applied to solidified/stabilised waste. Waste Manag. **27**, 1638–1647 (2007)
125. Corvisier, J., Bonvalot, A.F., Lagneau, V., Chiquet, P., Renard, S., Sterpenich, J., Pironon, J.: Impact of co-injected gases on CO2 storage sites: Geochemical modeling of experimental results. Proceedings of the International Conference on Greenhouse Gas Technology 11, vol. 37, pp. 3699–3710. Energy Procedia, Kyoto (2013)
126. Meeussen, J.C.: ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. Environ. Sci. Technol. **37**, 1175–1182 (2003)
127. Farmer, J.G., Graham, M.C., Thomas, R.P., Licona-Manzur, C., Paterson, E., Campbell, C.D., Geelhoed, J.S., Lumsdon, D.G., Meeussen, J.C.L., Roe, M.J., Conner, A., Fallick, A.E., Bewley, R.J.F.: Assessment and modelling of the environmental chemistry and potential for remediative treatment of chromium-contaminated land. Environ. Geochem. Health **21**, 331–33 (1999)
128. Geelhoed, J.S., Meeussen, J.C.L., Hillier, S., Lumsdon, D.G., Thomas, R.P., Farmer, J.G., Paterson, E.: Identification and geochemical modeling of processes controlling leaching of Cr(VI) and other major elements from chromite ore processing residue. Geochim. Cosmochim. Acta **66**, 3927–3942 (2002)
129. Filius, J.D., Lumsdon, D.G., Meeussen, J.C.L., Hiemstra, T., Van Riemsdijk, W.H.: Adsorption of fulvic acid on goethite. Geochim. Cosmochim. Acta **64**, 51–60 (2000)
130. Weng, L., Hiemstra, T., Meeussen, J.C.L., Koopal, L., Van Riemsdijk, W.H.: Interactions of calcium and fulvic acid at the goethite-water interface. Geochim. Cosmochim. Acta **69**, 325–339 (2005)

131. Van Riemsdijk, W.H., Koopal, L.K., Kinniburgh, D.G., Benedetti, M.F., Weng, L.: Modeling the interactions between humics, ions, and mineral surfaces. Environ. Sci. Technol. **40**, 7473–7480 (2006)
132. Vink, J.P.M., Meeussen, J.C.L.: BIOCHEM–ORCHESTRA: A tool for evaluating chemical speciation and ecotoxicological impacts of heavy metals on river flood plain systems. Environ. Pollut. **148**, 833–841 (2007)
133. Nowack, B., Mayer, K.U., Oswald, S.E., Van Beinum, W., Appelo, C.A.J., Jacques, D., Seuntjens, P.: Verification and intercomparison of reactive transport codes to describe root-uptake. Plant Soil **285**, 305–321 (2006)
134. Van der Sloot, H.A., van Zomeren, A.: Characterisation leaching tests and associated geochemical speciation modelling to assess long term release behaviour from extractive wastes. Mine Water Environ. **31**, 92–103 (2012)
135. Brown, K.G., Arnold, J., Sarkar, S., Flach, G., van der Sloot, H., Meeussen, J.C.L., Kosson, D.S.: Modeling carbonation of high-level waste tank integrity and closure. In EPJ Web of Conferences 56, 05003, EDP Sciences (2013)
136. Sarkar, S., Kosson, D.S., Mahadevan, S., Meeussen, J.C.L., van der Sloot, H., Arnold, J.R., Brown, K.G.: Bayesian calibration of thermodynamic parameters for geochemical speciation modeling of cementitious materials. Cem. Concr. Res. **42**, 889–902 (2012)
137. Xu, T., Pruess, K.: Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 1, Methodology. Am. J. Sci. **301**, 16–33 (2001)
138. Xu, T., Sonnenthal, E., Spycher, N., Pruess, K.: TOUGHREACT - a simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic Media: Applications for geothermal injectivity and CO2 geologic sequestration. Comput. Geosci. **32**, 145–165 (2006)
139. Xu, T., Spycher, N., Sonnenthal, E., Zhang, G., Zheng, L., Pruess, K.: TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions. Comput. Geosci. **37**, 763–774 (2011)
140. Pruess, K., Oldenburg, C., Moridis, G.: TOUGH2 user's guide, version 2.0. Lawrence Berkeley Laboratory Report LBL-43134, Berkeley, CA, p. 192 (1999)
141. Finsterle, S., Sonnenthal, E.L., Spycher, N.: Advances in subsurface modeling: The TOUGH suite of simulators. Comput. Geosci. **65**, 2–12 (2014)
142. Pruess, K., Narasimhan, T.N.: On fluid reserves and the production of superheated steam from fractured, vapor-dominated geothermal reservoirs. J. Geophys. Res. **87**, 9329–9339 (1982)
143. Dobson, P.F., Salah, S., Spycher, N., Sonnenthal, E.L.: Simulations of water rock interactions in the Yellowstone geothermal system using TOUGHREACT. Geothermics **33**, 493–502 (2004)
144. Xu, T., Ontoy, Y., Molling, P., Spycher, N., Parini, M., Pruess, K.: Reactive transport modeling of injection well scaling and acidizing at the Tiwi field, Philippines. Geothermics **33**, 477–491 (2004)
145. Wanner, C., Peiffer, L., Sonnenthal, E.L., Spycher, N., Iovenitti, J., Kennedy, B.M.: Reactive transport modeling of the Dixie Valley geothermal area: Insights on flow and geothermometry. Geothermics **51**, 130–141 (2014)
146. Spycher, N., Sonnenthal, E.L., Apps, J.: Fluid flow and reactive transport around potential nuclear waste emplacement tunnels at Yucca Mountain, Nevada. J. Contam. Hydrol. **62–63**, 653–674 (2003)
147. Sonnenthal, E.L., Ito, A., Spycher, N., Yui, M., Apps, J., Sugita, Y., Conrad, M., Kawakami, S.: Approaches to modeling coupled thermal, hydrological, and chemical processes In the Drift Scale Heater Test at Yucca Mountain. Int. J. Rock. Mech. Min. Sci. **42**, 698–719 (2005)
148. Xu, T., Senger, R., Finsterle, S.: Corrosion-induced gas generation in a nuclear waste repository: Reactive geochemistry and multiphase flow effects. Appl. Geochem. **23**, 3423–3433 (2008)
149. Marty, N.C.M., Tournassat, C., Burnol, A., Giffaut, E., Gaucher, E.C.: Influence of reaction kinetics and mesh refinement on the numerical modelling of concrete/clay interactions. J. Hydrol. **364**, 58–72 (2009)
150. Xu, T., Apps, J.A., Pruess, K.: Mineral sequestration of carbon dioxide in a sandstone–shale system. Chem. Geol. **217**, 295–318 (2005)
151. Audigane, P., Gaus, I., Czernichowski-Lauriol, I., Pruess, K., Xu, T.: Two-dimensional reactive transport modeling of CO_2 injection in a saline aquifer at the Sleipner site. Am. J. Sci. **307**, 974–1008 (2007)
152. Aradóttir, E.S.P., Sonnenthal, E.L., Björnsson, G., Jónsson, H.: Multidimensional reactive transport modeling of CO_2 mineral sequestration in basalts at the Hellisheidi geothermal field, Iceland. Int. J. Greenh. Gas. Con. **9**, 24–40 (2012)
153. Zheng, L., Spycher, N., Birkholzer, J., Xu, T., Apps, J., Kharaka, Y.: On modeling the potential impacts of CO2 sequestration on shallow groundwater: Transport of organics and co-injected H2S by supercritical CO2 to shallow aquifers. Int. J. Greenh. Gas. Con. **14**, 113–127 (2013)
154. Dalkhaa, C., Shevalier, M., Nightingale, M.: Mayer, B.: 2-D reactive transport modeling of the fate of CO2 injected into a saline aquifer in the Wabamun Lake Area, Alberta, Canada. Appl. Geochem. **38**, 10–23 (2013)
155. Wu, Y., Ajo-Franklin, J.B., Spycher, N., Hubbard, S.S., Zhang, G., Williams, K.H., Taylor, J., Fujita, Y., Smith, R.: Geophysical monitoring and reactive transport modeling of ureolytically-driven calcium carbonate precipitation. Geochem. Trans. **12** (2011)
156. Meima, J.A., Graupner, T., Rammlmair, D.: Modeling the effect of stratification on cemented layer formation in sulfide-bearing mine tailings. Appl. Geochem. **27**, 124–137 (2012)
157. Bea, S.A., Wainwright, H., Spycher, N., Faybishenko, B., Hubbard, S.S., Denham, M.E.: Identifying key controls on the behavior of an acidic-U (VI) plume in the Savannah River Site using reactive transport modeling. J. Contam. Hydrol. **151**, 34–54 (2013)
158. Kim, J., Sonnenthal, E., Rutqvist, J.A.: A sequential implicit algorithm of chemo-thermo-poro-mechanics for fractured geothermal reservoirs. Computers and Geosciences (2014)
159. White, M.D., Oostrom, M.: STOMP subsurface transport over multiple phases version 4.0 user's guide. Pacific Northwest National Laboratory, Washington (2006)
160. White, M.D., McGrail, B.P.: STOMP subsurface transport over multiple phases version 1.0, Addendum: ECKEChem equilibrium-conservation-kinetic equation chemistry and reactive transport. PNNL-15482. Pacific Northwest National Laboratory, Washington (2005)
161. Fang, Y.L., Yabusaki, S.B., Yeh, G.T.: A general simulator for reaction-based biogeochemical processes. Comput. Geosci. **32**, 64–72 (2006)
162. Balay, S., Brown, J., Buschelman, K., Eijkhout, V., Gropp, W.D., Kaushik, D., Knepley, M.G., Curfman McInnes, L., Smith, B.F., Zhang, H.: PETSc Users Manual, ANL–95/11 – revision 3.4. Argonne National Laboratory (2013)
163. Nieplocha, J., Palmer, B., Tipparaju, V., Krishnan, M., Trease, H., Apra, E.: Advances, applications and performance of the Global Arrays Shared Memory Programming Toolkit. Int. J. High Perform. Comput. Appl. **20**, 203–231 (2006)
164. Yeh, G.T., Tripathi, V.S.: HYDROGEOCHEM: A coupled model of HYDROlogical transport and GEOCHEMical equilibrium of multi component systems, ORNL 6371, Oak Ridge National

Laboratory, p. 37831. Oak Ridge National Laboratory, Oak Ridge (1990)

165. Yeh, G.T., Siegel, M.D., Li, M.H.: Numerical modeling of coupled fluid Fflows and reactive transport including fast and slow chemical reactions. J. Contam. Hydrol. **379–390**(2001), 47 (2001)
166. Yeh, G.T., Li, Y., Jardine, P.M., Burgos, W.D., Fang, Y.L., Li, M.H., Siegel, M.D.: HYDROGEOCHEM 4.0: A coupled model of fluid flow, thermal transport, and HYDROGEOCHEMical transport through saturated unsaturated media Version 4.0. ORNL/TM-2004/103, p. 37831. Oak Ridge National Laboratory, Oak Ridge (2004)
167. Yeh, G.T., Sun, J.T., Jardine, P.M., Burgos, W.D., Fang, Y.L., Li, M.H., Siegel, M.D.: HYDROGEOCHEM 5.0: A three dimensional model of coupled fluid flow, thermal transport, and HYDROGEOCHEMical transport through variably saturated conditions version 5.0. ORNL/TM-2004/107, p. 37831. Oak Ridge National Laboratory, Oak Ridge (2004)
168. Yeh, G.T., Tsai, C.H.: HYDROGEOCHEM 6.0: A two-dimensional model of coupled fluid flow, thermal transport, geomechanics, and HYDROGEOCHEMical transport through multiple phase systems version 6.0 (FACTM2D: A Model for multi-phase flow analysis and reactive chemical transport, thermal transport, and mechanics simulation, 2-dimensional version) - theoretical basis and numerical approximation. Graduate Institute of Applied Geology, National Central University, Jhongli (2013)
169. Yeh, G.T., Tsai, C.H., Ni, C.F.: HYDROGEOCHEM 6.0: A model to couple thermal-hydrology-mechanics-chemical (THMC) processes user guide. Graduate Institute of Applied Geology, National Central University, Jhongli (2013)
170. Yeh, G.T., Fang, Y.L., Zhang, F., Sun, J.T., Li, Y., Li, M.H., Siegel, M.D.: Numerical modeling of coupled fluid flow and thermal and reactive biogeochemical transport in porous and fractured media. Comput. Geosci. **14**, 149–170 (2010)
171. Yeh, G.T., Tripathi, V.J., Gwo, J.P., Cheng, H.P., Cheng, R.J., Salvage, K.M., Li, M.H., Fang, Y.L., Li, Y., Sun, J.T., Zhang, F., Siegel, M.D.: Chapter 1: HYDROGEOCGEM: A coupled model of variably saturated flow, thermal transport, and reactive biogeochemical transport. Groundwater reactive transport models. In: Zhang, F., Yeh, G.T., Parker, J.C. (eds.) Bentham e-Books. Bentham Science Publishers (2012). http://www.bentham.org
172. Smith, J.M.: Chemical engineering kinetics, p. 676. R. R. Donnelley & Sons Company (1981)
173. Chilakapati, A., Ginn, T., Szecsody, J.: An analysis of complex reaction networks in groundwater modeling. Water Resour. Res. **34**, 1767–1780 (1998)
174. Fang, Y., Yeh, G.T., Burgos, W.D.: A New Paradigm to model reaction-based biogeochemical processes. Water Resour. Res. **39**, 1083–1108 (2003)
175. Kräutle, S., Knabner, P.: A reduction scheme for coupled multicomponent transport-reaction problems in porous media: Generalization to problems with heterogeneous equilibrium reactions. Water Resour. Res. **43**, W03429 (2007). doi:10.1029/2005WR004465
176. Yeh, G.T., Tsai, C.H., Fang, Y., Yabusaki, S., Li, M.H.: BIOGEOCHEM 1.5: A numerical model to simulate BIOGEOCHEMical reactions under multiple phase system. Graduate Institute of Applied Geology, National Central University, Jhongli (2014)
177. Yeh, G.T., Tsai, C.H.: User's manual for BIOGEOCHEM 1.5. Graduate Institute of Applied Geology, National Central University, Jhongli (2014)
178. Yeh, G.T., Tripathi, V.S.: A critical evaluation of recent developments of hydrogeochemical transport models of reactive multi-chemical components. Water Resour. Res. **25**, 93–108 (1989)
179. Liu, I.-S., Cipolatti, R.A., Rincon, M.A.: Successive linear approximation for finite elasticity. Comput. Appl. Math. **29**, 465–478 (2010)
180. Yeh, G.T., Tripathi, V.S.: A model for simulating transport of reactive multispecies components: Model development and demonstration. Water Resour. Res. **27**, 3075–3094 (1991)
181. Gwo, J.P., D'Azevedo, E.F., Frenzel, H., Mayes, M., Yeh, G.T., Jardine, P.M., Salvage, K.M., Hoffman, F.M.: HBGC123D: A high performance computer model of coupled hydrogeological and bigeochemical processes. Comput. Geosci. **27**, 1231–1242 (2001)
182. Yeh, G.T., Gwo, J.P., Siegel, M.D., Li, M.H., Fang, Y.L., Zhang, F., Luo, W.S., Yabusaki, S.B.: Innovative mathematical modeling in environmental remediation. J. Environ. Radioact. (2011). doi:10.1016/j.jenvrad.2011.06.010
183. Kent, D.B., Davis, J.A., Anderson, L.C.D., Rea, B.A., Waite, T.D.: Transport of chromium and selenium in the suboxic zone of a shallow aquifer: Influence of redox and adsorption reactions. Water Resour. Res. **30**, 1099–1114 (1994)
184. Abrams, R.H.: A compartmentalized approach to simulating redox zones in contaminated aquifers. PhD Dissertation, Department of Geological and Environmental Sciences, Stanford University, Palo Alto, California (1999)
185. Bahr, J.M.: Keating, E.H.:. Redox geochemistry of shallow groundwater discharging to Allequash Creek in northern Wisconsin. WRC GRR 95-08. Water Resources Center, University of Wisconsin-Madison, p. 41 (1995)
186. Tournassat, C., Appelo, C.A.J.: Modelling approaches for anion-exclusion in compacted Na-bentonite. Geochim. Cosmochim. Acta **75**, 3698–3710 (2011)
187. Steefel, C.I., Van Cappellen, P.: A new kinetic approach to modeling water-rock interaction: The role of nucleation, precursors, and Ostwald ripening. Geochim. Cosmochim. Acta **54**, 2657–2677 (1990)
188. Steefel, C.I., Lasaga, A.C.: A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. Am. J. Sci. **294**, 529–592 (1994)
189. Steefel, C.I., Lichtner, P.C.: Diffusion and reaction in rock matrix bordering a hyperalkaline fluid-filled fracture. Geochim. Cosmochim. Acta **58**, 3592–3612 (1994)
190. Steefel, C.I., Lichtner, P.C.: Multicomponent reactive transport in discrete fractures: I. Controls on reaction front geometry. J. Hydrol. **209**, 186–199 (1998)
191. Steefel, C.I., Lichtner, P.C.: Multicomponent reactive transport in discrete fractures: II. Infiltration of hyperalkaline groundwater at Maqarin, Jordan, a natural analogue site. J. Hydrol. **209**, 200–224 (1998)
192. Giambalvo, E.R., Steefel, C.I., Fisher, A.T., Rosenberg, N.D., Wheat, C.G.: Effect of fluid-sediment reaction on hydrothermal fluxes of major elements, eastern flank of the Juan de Fuca Ridge. Geochim. Cosmochim. Acta **66**, 1739–1757 (2002)
193. Maher, K., Steefel, C.I., DePaolo, D., Viani, B.: The mineral dissolution rate conundrum: Insights from reactive transport modeling of U isotopes and pore fluid chemistry in marine sediments. Geochim. Cosmochim. Acta **70**, 337–363 (2006)

194. Maher, K., Steefel, C.I., White, A.F., Stonestrom, D.A.: The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. Geochim. Cosmochim. Acta **73**, 2804–2831 (2009)
195. Navarre-Sitchler, A., Steefel, C.I., Sak, P.B., Brantley, S.L.: A reactive transport model for weathering rind formation on basalt. Geochim. Cosmochim. Acta **75**, 7644–7667 (2011)
196. Navarre-Sitchler, A., Steefel, C.I., Yang, L., Tomutsa, L., Brantley, S.L.: Evolution of porosity and diffusivity associated with chemical weathering of a basalt clast. J. Geophys. Res., 114 (2009). doi:10.1029/2008JF001060
197. Li, L., Gawande, N., Kowalsky, M.B., Steefel, C.I., Hubbard, S.S.: Physicochemical heterogeneity controls on uranium bioreduction rates at the field scale. Environ. Sci. Technol. **45**, 9959–9966 (2011)
198. Li, L., Steefel, C.I., Kowalsky, M.B., Englert, A., Hubbard, S.S.: Effects of physical and geochemical heterogeneities on mineral transformation and biomass accumulation during uranium bioremediation at Rifle, Colorado. J. Contam. Hydrol. **11**, 45–63 (2010)
199. Li, L., Steefel, C.I., Williams, K.H., Wilkins, M.J., Hubbard, S.S.: Mineral transformation and biomass accumulation during uranium bioremediation, Rifle, Colorado. Environ. Sci. Technol. **43**, 5429–5435 (2009)
200. Druhan, J.L., Steefel, C.I., Molins, S., Williams, K.H., Conrad, M.E., DePaolo, D.J.: Timing the onset of sulfate reduction over multiple subsurface acetate amendments by measurement and modeling of sulfur isotope fraction. Environ. Sci. Technol. **46**, 8895–8902 (2012)
201. Druhan, J.L., Steefel, C.I., Conrad, M.E., DePaolo, D.J.: A large column analog experiment of stable isotope variations during reactive transport: I. A comprehensive model of sulfur cycling and δ 34S fractionation. Geochim. Cosmochim. Acta **124**, 366–393 (2014)
202. Mayer, K.U., Frind, E.O., Blowes, D.W.: Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. Water Resour. Res. **38**, 1174 (2002). doi:10:1029/2001WR000862
203. Cheng, L.: Dual porosity reactive transport modeling, PhD thesis. University of Sheffield, UK (2006)
204. Cheng, L., Lerner, D., Thornton, S., Mayer, K.U.: Managing MTBE attenuation in a dual porosity chalk aquifer – field observations and modelling results. Proceedings of ModelCARE 2009 Groundwater and the Environment, p. 341. IAHS Publishing, Wuhan (2009)
205. Amos, R.T., Mayer, K.U.: Investigating the role of gas bubble formation and entrapment in contaminated aquifers: Reactive transport modeling. J. Contam. Hydrol. **87**, 123–154 (2006)
206. Amos, R.T., Mayer, K.U.: Investigating ebullition in a sand column using dissolved gas analysis and reactive transport modelling, Environ. Sci. Technol. **40**, 5361–5367 (2006)
207. Molins, S., Mayer, K.U., Scheutz, C., Kjeldsen, P.: Role of transport mechanisms in the attenuation of landfill gas in cover soils: A multicomponent modelling study. J. Environ. Qual. **37**, 459–468 (2008)
208. Molins, S., Mayer, K.U., Amos, R.T., Bekins, B.A.: Vadose zone attenuation of organic compounds at a crude oil spill site - Interactions between biogeochemical reactions and multicomponent gas transport. J. Contam. Hydrol. **112**, 15–29 (2010)
209. Henderson, T., Mayer, K.U., Parker, B., Al, T.: Three-dimensional density-dependent flow and multicomponent reactive transport modeling of chlorinated solvent oxidation by potassium permanganate. J. Contam. Hydrol. **106**, 195–211 (2009)
210. Bea, S.A., Mayer, K.U., MacQuarrie, K.T.B.: Modelling reactive transport in sedimentary rock environments - Phase II MIN3P-THCm code enhancements and illustrative simulations for a glaciation scenario. Technical report: NWMO TR-2011-13 (2011)
211. Harvie, C.E., Moller, N., Weare, J.H.: The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25 °C. Geochim. Cosmochim. Acta **48**, 723–751 (1984)
212. Pitzer, K.S.: Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. **77**, 268–277 (1973)
213. Monnin, C.: Density calculation and concentration scale conversions for natural waters. Comput. Geosci. **20**, 1435–1445 (1994)
214. Neuzil, C.: Hydromechanical coupling in geologic processes. Hydrogeol. J. **11**, 41–83 (2003)
215. Bea, S., Wilson, S., Mayer, K.U., Dipple, G., Power, I., Gamazo, P.: Reactive transport modeling of natural carbon sequestration in ultramafic mine tailings. Vadose Zone J. **11**, 1–17 (2012)
216. Sihota, N.J., Mayer, K.U.: Characterizing vadose zone hydrocarbon biodegradation using CO_2-effluxes, isotopes, and reactive transport modeling. Vadose Zone J., 11 (2012). doi:10.2136/vzj2011.0204
217. Miller, G.R., Rubin, Y., Mayer, K.U., Benito, P.H.: Modeling vadose zone processes during land application of food-processing waste water in California's Central Valley. J. Environ. Qual. **37**, 43–57 (2008)
218. Gérard, F., Tinsley, M., Mayer, K.U.: Preferential flow revealed by hydrologic modeling based on predicted hydraulic properties and intensive water content monitoring. Soil Sci. Soc. Am. J. **68**, 1526–1538 (2004)
219. Lichtner, P.C., Hammond, G.E., Lu, C., Karra, S., Bisht, G., Andre, B., Mills, R.T., Kumar, J.: PFLOTRAN User manual: A Massively Parallel Reactive Flow and Transport Model for Describing Surface and Subsurface Processes (2013)
220. Goode, D.J.: Direct simulation of groundwater age. Water Resour. Res. **32**, 289–296 (1996)
221. Hammond, G.E., Lichtner, P.C.: Field-scale model for the natural attenuation of uranium at the Hanford 300 area using high performance computing. Wat. Res. Res **46**, 1–31 (2010)
222. Lichtner, P.C., Karra, S.: Modeling multiscale-multiphase-multicomponent reactive flows in porous media: Application to CO2 sequestration and enhanced geothermal energy using PFLOTRAN. In: Al-Khoury, R., Bundschuh, J. (eds.) Computational Models for CO2 Geo-sequestration & Compressed Air Energy Storage, pp. 81–136. CRC Press (2014)
223. Karra, S., Painter, S.L., Lichtner, P.C.: Three-phase numerical model for subsurface hydrology in permafrost-affected regions. Cryosphere Discuss. **8**, 149–185 (2014)
224. de Vries, L.M., Molinero, J., Ebrahimi, H., Svensson, U., Lichtner, P.: High performance reactive transport simulation of hyperalkaline plume migration in fractured rocks. Mineral. Mag. **77**, 982 (2013)
225. Navarre-Sitchler, A.K., Maxwell, R.M., Siirila, E.R., Hammond, G.E., Lichtner, P.C.: Elucidating geochemical response of shallow heterogeneous aquifers to CO2 leakage using high-performance computing: Implications for monitoring of CO2 sequestration. Adv. Water Resour. **53**, 45–55 (2013)
226. Steefel, C.I., DePaolo, D., Lichtner, P.C.: Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. Earth Planet. Sci. Lett. **240**, 539–558 (2005)

227. Gibson, B.D., Amos, R.T., Blowes, D.W.: S-34/S-32 fractionation during sulfate reduction in groundwater treatment systems: Reactive transport modeling. Env. Sci. Technol. **45**, 2863–2870 (2011)
228. Greskowiak, J., Prommer, J.H., Liu, C., Post, V.E.A., Ma, R., Zheng, C., Zheng, C., Zachara, J.M.: Comparison of parameter sensitivities between a laboratory and field-scale model of uranium transport in a dual domain, distributed rate reactive system. Water Resour. Res. **46**, 9: W09509 (2010)
229. Doherty, J.: PEST: A unique computer program for model-independent parameter optimisation. Water Down Under 94: Groundwater/Surface Hydrology Common Interest Papers; Preprints of Papers, p. 551 (1994)