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Code Verification and Confidence-Building

Groundwater Working Group

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1. Purpose

This document described the current status of verification and confidence building activities for the four simulation codes used for groundwater flow and transport simulations in the NRAP project. This is meant to be a 'living document' which will evolve as the verification suites expand and the models are tested against new field and laboratory experiments. Documenting these activities will enable the simulation teams at different laboratories to share verification problems, to benchmark against other codes. It will also help stakeholders understand the testing process and to gain confidence in model results.

2. Background

One of the areas of concerns for geologic CO_2 sequestration is the potential of leakage of CO_2 and brine from deeper storage reservoirs to shallow groundwater resources. The groundwater impacts working group, part of the National Risk Assessment Partnership (NRAP), is developing simulations to predict the impacts of leaks on aquifers. Four simulation codes are being used: TOUGHREACT (Xu and Pruess, 2001), NUFT (Nitao, 1998), STOMP (White et al., 2012), and FEHM (Zyvoloski et al., 2011). Each DOE national laboratory (LBNL, LLNL, PNNL and LANL) employs a suite of test problems to verify the accuracy of their codes. This paper summarizes that subset of each verification suite with chemistry and physics relevant to NRAP and identifies opportunities for individual codes to expand their suite of test problems.

Each of the four codes (TOUGHREACT, NUFT, STOMP, and FEHM) has the capability to simulate multiphase/multi-component fluid flow and reactive transport in porous and fractured media. These codes can be applied to one-, two- or three-dimensional models with physical and chemical heterogeneity and can accommodate any number of chemical species present in liquid, gas, and solid phases. A variety of subsurface thermal, physical, and chemical processes are considered in these codes under a wide range of conditions of pressure, temperature, water saturation, ionic strength, and pH and Eh.

For the purposes of this summary, we define two categories of model confidence building. The first, verification, is defined as a demonstration that the code is solving the equations of fluid flow and/or reactive transport properly. Verification can be accomplished either by comparison to an analytical solution of the equations or by benchmarking model results against another code. Benchmarking is often the only option for complex physics/chemistry problems. The second category includes exercises where it has been demonstrated that the code can reproduce field-scale or laboratory-scale measurements relevant to NRAP problems, such as CO2 partial pressures or saturations, and aqueous chemistry in CO_2-rich or high-salinity environments.

3. Simulation codes

3.1. TOUGHREACT (LLBL)

TOUGHREACT has been undergone extensive verification and validation over the course of code development. Verification of non-isothermal multiphase flow is given by Pruess (1987; 1991) and Pruess et al. (1996). The verification and validation of reactive transport was mainly described in Xu and Pruess (1998), Xu et al. (2005b) and Xu et al. (2012). The program has been verified against analytical solution and validated against model results of other codes and measured data. Several verification and validation examples (related to CO2 flow and reactive transport) are given below.

V1: Reactive transport with kinetic mineral dissolution against analytical solution. The verification case considers 1-D transport of two hypothetical species A and B, which originate from the dissolution of a mineral phase Abs, Abs = A + B, in a semi-infinite water saturated medium under a steady uniform velocity flow regime. This problem can be solved analytically for both equilibrium and kinetic conditions. The comparison between model results and analytical solution for this case is given in Xu and Pruess (1998).

V2: Reactive transport with adsorption (linear Kd) and decay against analytical solution. A 1-D homogeneous fully water-saturated porous medium is considered, using the following parameters: a porosity of 0.1, a pore velocity v of 0.1 m/day, a solid density of 2600 kg/m^3, a distribution coefficient Kd of 0.042735 l/kg, which corresponds to a retardation factor R of 2, and a half-life $t_{1/2}$ of 20 days. The flow system is a cylindrical, horizontal porous medium with cross-sectional area of 1 m^2 and 12 m length, divided into 60 grid blocks of 0.2 m thickness. A total of four species are simulated in a single run. Species 1 is not subject to adsorption (R = 1) and decay ($t_{1/2}$ = inifinite). Species 2 has a R = 2 and a $t_{1/2}$ = infinite. Species 3 has a R = 1 and a $t_{1/2}$ = 20 days. Species 4 has a R = 2 and a $t_{1/2}$ = 20 days. The inlet concentrations are set equal to 10-4 mol/l for all four species. An analytical solution for this problem is from Javandel et al. (1984). Details of this verification case are given in Xu et al. (2005b).

V3: Reactive transport with pyrite oxidation in a variably saturated medium against model results of other code. In this case a prototype for oxidative weathering processes of pyrite in an unsaturated-saturated medium was simulated with TOUGHREACT and compared with TOUGH2-CHEM (White, 1995). A vertical column is modeled, which extends from the atmosphere though an unsaturated zone and below the water table. Oxygen is supplied to the top of the column as a dissolved species in infiltrating rainwaters and is also transported by gaseous diffusion from the land surface boundary. The initial flow conditions are set by specifying the rate of water infiltration into the top of the model and a constant pressure of 3.5 bar at the bottom. A close match between model results from two codes was obtained and details of this validation case are given in Xu and Pruess (1998).

V4: Reactive transport with cation exchange and calcite dissolution/precipitation against measured data. NaHCO3 type waters in coastal plain aquifers of the eastern United States have been related to freshening of the aquifer (Chapelle and Knobel, 1983). These investigators depict major cation patterns as a function of flow length in the Aquia aquifer (Maryland). The water quality in this aquifer shows zonal bands with changes in concentrations of major cations that have been attributed to cation exchange and calcite dissolution/precipitation. TOUGHREACT simulation was conducted, aiming to validate the model applicability to field-scale ambient problems. The aquifer is

bounded to the east by a change in facies. The prepumping hydraulic head distribution suggests a confined aquifer in the upstream half and gradual loss of water in the downstream part of the aquifer. Leakage probably occurs via Pleistocene channels that cut through the confining beds. The hydrological conditions have been modeled assuming a one-dimensional flow tube with recharge at x = 0, and with seepage into the confining layers evenly distributed over the second half of the flow tube. The comparison of model results an measured data from Chapelle and Knobel (1983) is given in Xu et al. (2012).

3.2. NUFT (LLNL)

NUFT (Nonisothermal Unsaturated-saturated Flow and Transport) is a highly flexible computer software package using the C++ language for modeling multiphase, multi-component heat and mass flow and reactive transport in unsaturated and saturated porous media (Nitao, 1998; Hao et al., 2012). This computer code includes several sub-modules for a variety of flow and reactive transport processes in porous and fractured media. Among those sub-modules, USNT module (fully coupled unsaturated multiple phases, multiple components flow with isothermal and nonisothermal options) and TRANS module (geochemical multiphase transport) are used in NRAP project for evaluating the impact of CO_2 leakage in groundwater aquifers. The code has been verified, validated, and widely used for modeling of subsurface multiphase flow and reactive transport processes in many projects. Application examples include geological disposal of nuclear waste (Sun et al., 2010), CO_2 geological sequestration (Carroll et al., 2009), groundwater remediation (Carrigan and Nitao, 2000), and multiphase flow and transport (Fernandez et al., 1998). Here we only provide two benchmark examples for transport and first-order reactions in a one-dimensional column.

V**1: Transport in one dimension**. The generalized kinetic reaction can be specified to express the first-order sequential reactions using a small number of saturation constant, and a large number of inhibition constant, relatively to the concentration magnitude (Sun et al., 2012). Then, the multiple-Monod formulation of reactions with catalysis/inhibition are simplified in first-order sequential format. Closed-form solutions of the transport coupled with the first-order sequential reactions may be available or easily derived for verification purposes. In order to test transport and reactions in the USNT module, a one-dimensional reactive transport problem with first-order sequential reactions is considered. Uniform and constant velocity and dispersivity are assumed. The boundary conditions are referred to Bear (2000).

Transport processes are calibrated first using the analytical solution of (Bear, 2000) assuming zero reaction rate. Figure 1 shows the comparison between the analytical solution and NUFT (Nitao, 1998) simulations at 1, 2, and 3 years along the column. Both analytical and numerical solutions were computed for a column of length 150 m discretized using 75 evenly spaced nodal points. A slight difference at the outlet is due to the boundary effect in the numerical model.

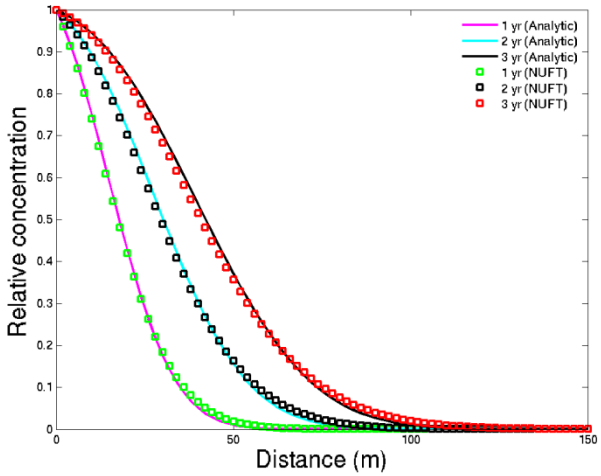

Figure 1: Concentration profiles of a single species in a one-dimensional column simulated using the analytical and numerical solutions. v = 0.0031 m/d and D=10.0 m.

V2: Transport coupled with first-order chain reactions. The transport of four species with four-step sequential first-order reactions is considered to calibrate the reaction module in the NUFT USNT code,

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow.$$

The final product of the fourth reaction is not considered. The equations of reactive transport and initial and boundary conditions are referred to Sun et al. (1999). When the transport time is sufficiently large, the analytical solution of the steady-state concentrations is provided by Petersen and Sun (2000). Figure 2 indicates good agreement of the spatial concentrations simulated using the analytical solution and the NUFT code.

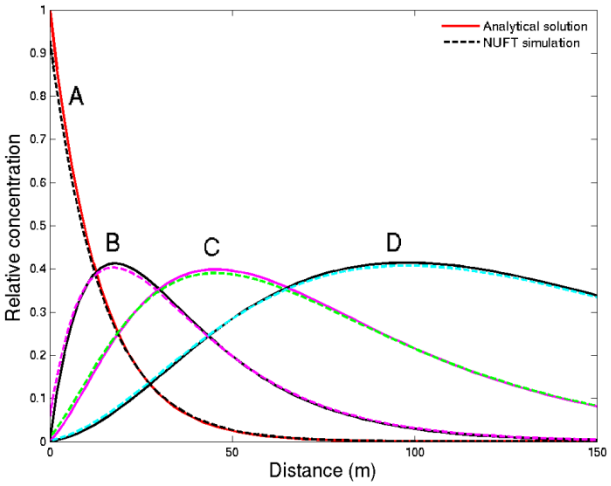

Figure 2: Concentration profiles of three sequential first-order decaying species in a one-dimensional column simulated using the analytical solution and NUFT code. v = 0.0031 m/d, D =5.0 m, k_1 = 0.0031, $k_2 = 0.5k_1$, $k_3 = 0.25k_1$, and $k_4 = 0.125k_1$ 1/d.

3.3. STOMP (PNNL)

STOMP (Subsurface Transport Over Multiple Phases) has two CO_2 simulators: STOMP-CO2 and STOMP-CO2e, which are developed at the Pacific Northwest National Laboratory[1] (PNNL) (using a mixture of Fortran 77/90 language) for conducting research associated with geologic sequestration of CO_2 that includes the thermo-chemistry of supercritical CO_2-brine mixtures, mineralization kinetics, leakage and micro-seepage of CO_2, and new materials for CO_2 capture.

The STOMP-CO2 and -CO2e simulators solve conservation equations for component mass (i.e., water, CO_2, and salt) and energy on a structured orthogonal grid. In their native form the conservation equations are expressed as partial differential equations. Each conservation equation is solved for a primary variable. The primary variables must be chosen to be independent and completely define the state of the system. All secondary variables must be determined from the primary variable set. The STOMP-CO2 simulator has three primary variables and the STOMP-CO2e simulator has four primary variables, with the extra primary variable being from the energy conservation equation. Because of phase appearances and disappearances, three sets of primary variables are used by STOMP-CO2 and -CO2e. A primary variable switching scheme is used to transition between primary variable sets with phase condition transitions. To ensure smooth transitions across phases, the primary variable switching occurs between Newton-Raphson iterations within a single time step. The constitutive equations relate the primary variables with all of the secondary variables. Secondary variables include thermodynamic and transport properties and phase compositions. The collection of constitutive equations that describe the phase conditions, phase compositions, and phase densities, assuming phase equilibria, will be referred to as the equation of state. Following are a series of benchmark problems for verifying the STOMP-CO2 and -CO2e simulators, including those with geochemistry and geomechanics.

V1: Radial flow of supercritical CO_2 from an injection well. Radial flow of injected supercritical CO_2 into simplified fresh-water and saline aquifers is compared. This problem addresses two-fluid flow of CO_2 and aqueous for a simplified flow geometry and aquifer properties. A constant mass injection rate of CO_2 is applied from a line source at the center of the infinite radial domain into an aquifer with homogeneous and isotropic hydrologic properties. Gravity and inertial effects are ignored by using a one-dimensional radial computational domain. The problem has a similarity solution, where dependence on the radial distance (r) and time (t), is replaced by the similarity variable ($x = r^2/t$), (O'Sullivan 1981; Doughty and Pruess 1992).

V2: Discharge of sequestered CO_2 along a fault zone. Loss of CO_2 from a deep fresh-water aquifer through a leaky fault is investigated. This problem addresses two-fluid flow of CO_2 and aqueous for a simplified, one-dimensional vertical flow geometry (Figure 3). The problem is designed to investigate the transport of CO_2 from the disposal reservoir to a shallow aquifer 500 m above, through an intersecting vertical fault. The vertical fault is idealized using a one-dimensional geometry and constant pressure boundary conditions (Pruess and Garcia 2002).

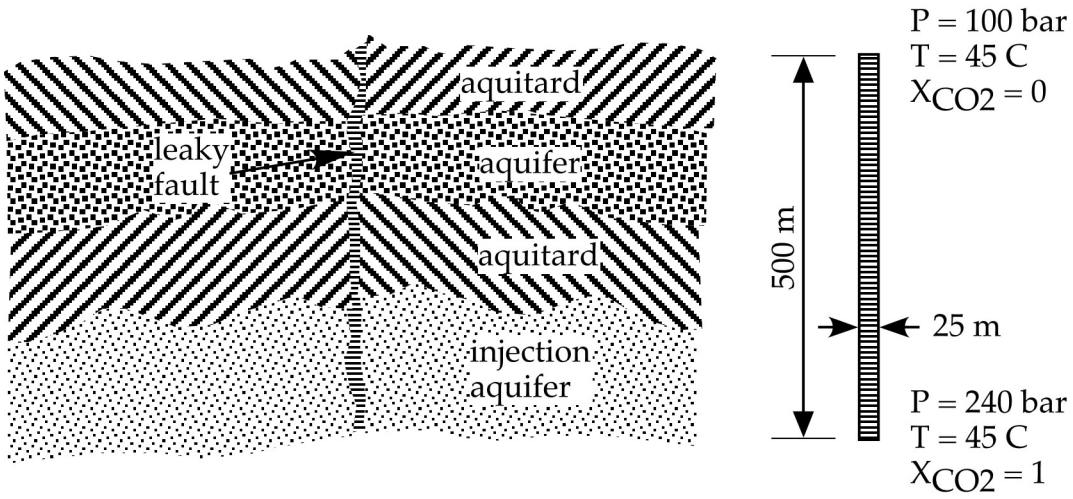

Figure 3: Schematic of fault-connected aquifers and idealized fault with boundary conditions (from Pruess et al., 2002 and White at el., 2012)

V3: Mineral trapping in a glauconitic sandstone aquifer. This problem addresses geochemical effects of CO_2 injection into a glauconitic sandstone aquifer, and analyzes the impact of CO_2 immobilization through carbonate precipitation. Batch reaction modeling of the geochemical evolution of this aquifer is performed in the presence of CO_2 at high pressure. The problem is based on (Gunter et al. 1997), who modeled water-rock reactions when CO_2 is injected into a glauconitic sandstone aquifer in the Alberta Sedimentary Basin, Canada.

V4: CO_2 injection into a 2-dimensional layered brine formation. Pressure and buoyancy driven migration of CO_2 injected into a layered formation that is representative of the Sleipner Vest field in the Norwegian sector of the North Sea is investigated. A key assumption for the problem, as posed, was isothermal conditions at the formation temperature of 37˚C; therefore, STOMP-CO2 was executed for these simulations. The problem involves a constant mass rate injection of scCO_2 into a layered saline formation comprising sands and shales. There are five sand layers and four thinner shale layers, whose intrinsic permeability is lower than those of the sands, as shown in Figure 4.

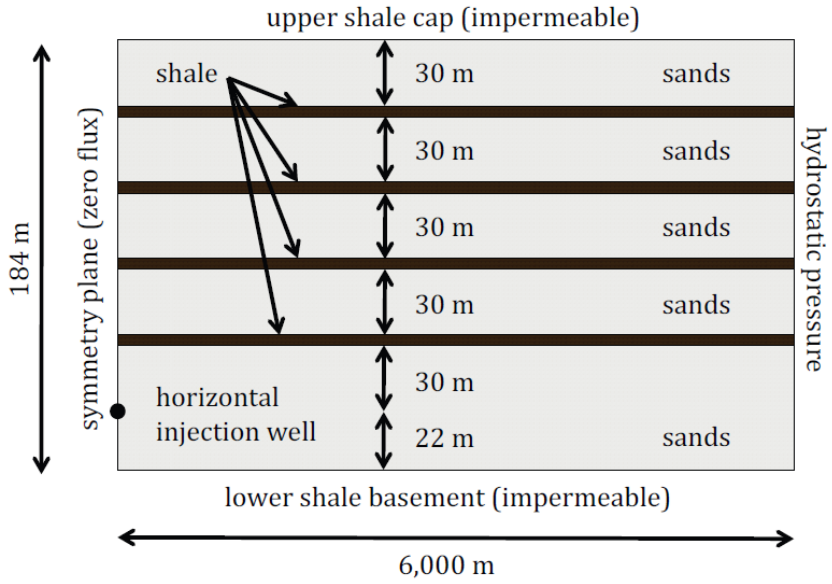

Figure 4: Schematic of injection reservoir, showing location of the injection well and lithology (from White at el., 2012)

V5: CO_2 plume evolution and leakage through an abandoned well. This problem involves the injection of $scCO_2$ into a saline formation with an abandoned well that provides a conduit for CO_2 migration between lower and upper permeable layers. Two scenarios are considered: 1) deep conditions where the entire domain remains under supercritical temperature and pressure conditions for CO_2, and 2) shallow conditions where the upper portion of the domain is outside of supercritical temperature and pressure conditions for CO_2. This problem is identical to Problem 1 from the series of problems developed at the University of Stuttgart (Ebigbo et al., 2007a,b), entitled "Numerical Investigations of CO_2 Sequestration in Geological Formations: Problem-Oriented Benchmarks." This problem was developed using analytical and semi-analytical solutions published by Nordbotten et al. (2004, 2005a,b). The deep scenario involves isothermal conditions and was executed with STOMP-CO2. The shallow scenario considered nonisothermal effects and was executed with STOMP-CO2e.

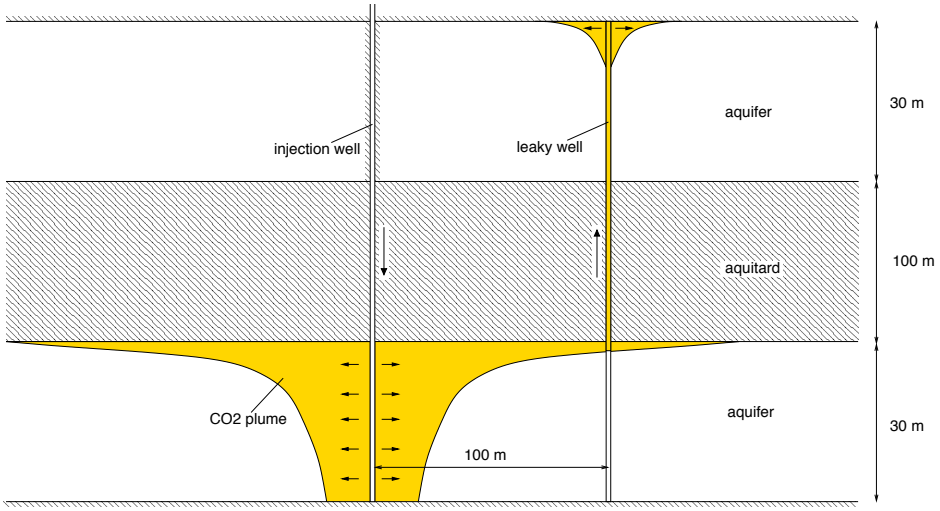

Figure 5: Problem domain from Ebigbo et al. (2007a,b)

3.4. FEHM (LANL)

FEHM (Finite Element Heat and Mass) is a numerical simulation code for subsurface transport processes. It models 3D, time-dependent, multiphase, multi-component, nonisothermal, reactive flow through porous and fractured media. It can accurately represent complex geologic structures and their effects on subsurface flow and transport. FEHM has been used to simulate groundwater and contaminant flow and transport in deep and shallow, fractured and non-fractured porous media throughout the US DOE complex. Subsurface physics has ranged from single fluid/single phase fluid flow when simulating basin scale groundwater aquifers to complex multi-fluid/multi-phase fluid flow that includes phase change with boiling and condensing in applications such as unsaturated zone surrounding nuclear waste storage facility or leakage of CO_2/brine through faults or wellbores. (https://fehm.lanl.gov/).

FEHM has been extensively verified against analytical solutions and validated against model results of other codes and measured data. Two benchmark examples related to CO_2 flow and reactive transport are given below.

V1: Radial flow of supercritical CO_2 from a production well.

FEHM verification is first conducted for several cases with water only or CO_2 only, since analytical solutions for multiphase flow problems are not available (Stauffer et al., 2013). A two-dimensional radial flow model is used, and the governing equation for the radial flow can be written as

$$\frac{\partial p}{\partial t} = \frac{k}{\phi \mu c_t} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial p}{\partial r} \right), \quad (1)$$

where p [Pa] is the pressure, k [m^2] is the permeability ϕ [-] is porosity, μ [Pa ·s] is the dynamic viscosity, c_t [Pa^{-1}] is the total compressibility, r [m] is the radial distance from the well, and t [s] is time.

The model configuration is shown in Figure 6. The model domain has a radius of 20 km and a height of 100 m. The reservoir with a thickness of 60 m is confined by low permeable confining layers. A production well of wellbore radius r_w is located on the left. Various boundary conditions are specified in different cases and the comparison results are presented in Figure 7.

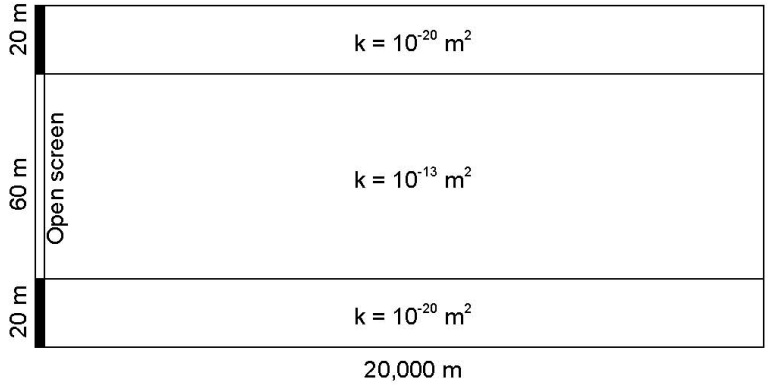

Figure 6: Problem configuration for two-dimensional radial flow (Stauffer et al., 2013)

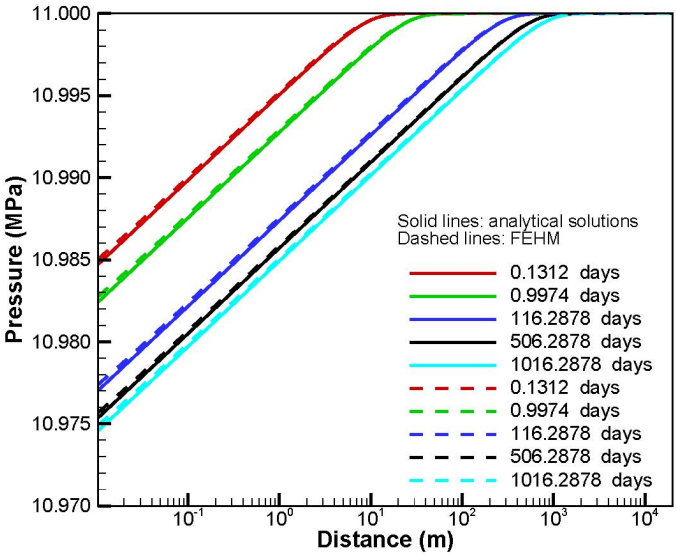

Figure 7: Comparisons of water pressure profiles derived from analytical solutions and FEHM simulations for several selected times (Stauffer et al., 2013).

V2: Transport of CO_2 along a fault zone. In this case the CO_2 leaked from a deep reservoir through a vertical fault is investigated. This problem was originally developed by Pruess and Garcia (2002) for two-fluid flow of CO_2 and aqueous in a simplified, one-dimensional vertical flow geometry (also see Figure 3).

The CO_2 is leaked from a storage reservoir which is confined by an aquitard of 500-m thickness, which is assumed that the confining layer is breached along a 25-m-wide fault zone (Fig. 3). The model is further simplified to be an one-dimensional section of 1-m thickness through the fault, and applying constant pressure and phase composition boundary conditions at the intersections of the fault zone with the storage aquifer (250 bar) and another aquifer (100 bar) overlying the aquitard. The temperature of the flow system is 40 ^{o}C constantly and the porosity of the fault zone is 0.35. The CO_2-water flow and transport processes are simulated with the CO_2 modular of FEHM. The simulated results are plotted in Figure 8, which shows the same transport behavior as that obtained by Pruess and Garcia (2002, Fig. 9). The good match of the FEHM results with the published results demonstrates that the accuracy of the CO_2 modular within FEHM is good for CO_2 multi-phase flow and transport modeling.

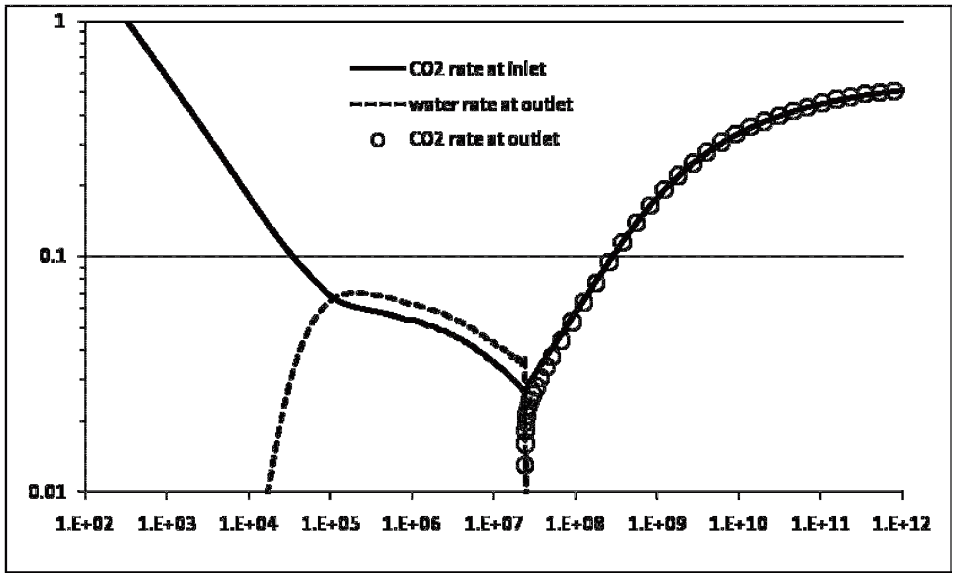

Figure 8: The simulated results of the CO_2 transport along the fault zone.

4. Summary

These problems are summarized in Tables 1 (Verification) and Tables 2 (Model confidence building).

Table 1. Verification (demonstration that equations are solved properly, using analytic solutions or other codes)

General reactive solute transport

		TOUGHREACT	FEHM	NUFT	STOMP
Kinetic mineral dissolution	Single phase	Analytic (Xu and Pruess, 1998)	Analytic (Engesgaard, 1991, Walsh et al., 1984)		Benchmark (Delany, Puigdomenech & Wolery 1986) Problem 1
Adsorption (kd)	Single phase	Analytic (Javandel et al. 1984)	Benchmark (SORBEQ (Robinson, 1993 and PDREACT (Valocchi et al., 1994)		Benchmark (Parkhurst and Appelo 1999) Example 15
Monod kinetics, catalysis/inhibition	Single phase			Analytic (Bear, 2000)	Benchmark (Parkhurst and Appelo 1999) Example 15
Cation exchange, mineral dissolution	Multi phase	Benchmark (TOUGH2-CHEM)			Benchmark (Parkhurst and Appelo 1999) Example 11
Surface complexation			N/A		Benchmark (Parkhurst and Appelo 1999) Example 8

CO_2 flow and transport

		TOUGH2	FEHM	NUFT	STOMP
Supercritical CO2 injection/radial flow	Single phase		Analytic (Stauffer et al., 2013)	Benchmark, Sun et al., 2013	
	Multi-phase				Analytic (Doughty and Pruess, 1992)
CO2 flow in a fault zone	Multi-phase		Benchmark (Pruess and Garcia, 2002)	Benchmark, Lu et al., 2013	Benchmark (Pruess and Garcia, 2002)
Leakage from an abandoned well	Multi-phase				Benchmark (Ebigbo 2007)

Table 2. Comparisons of model output with field-scale and laboratory data

General reactive solute transport

		TOUGH2	FEHM	NUFT	STOMP
Cation exchange, mineral dissolution	Single-phase	Chappelle and Knobel, 1983)			
Cation exchange	Single-phase		Viswanathan et al., 1998		

CO_2 flow and transport

		TOUGH2	FEHM	NUFT	STOMP
Mineral trapping	Multi-phase			Hao et al. (2013)	Gunter et al. (1997), Schaef et al. (2010)
Shallow groundwater chemistry changes at controlled release experiments	Single-phase	Zheng et al. (2012) Trautz et al., (2012)		Hao et al. (2013)	
Laboratory experiments exposing sediments to CO2	Single-phase		Viswanathan et al. (2012)		In progress
Shallow groundwater flow and transport in presence of naturally-occurring CO2	Multi-phase		Keating et al. (2012)		

5. Opportunities

The reactive transport capabilities of all four codes are fairly comprehensive and verified. There is not complete overlap in the specific verification problems used by each code, and so there are opportunities for each code to expand their verification suites. Only one code (STOMP) has a multi-phase reactive transport verification problem; the other codes might benefit from adding this problem to their suites.

The CO_2 flow and transport verification problems are more limited. Three of the codes (TOUGH2, FEHM, and NUFT) only have high pressure verification problems for supercritical CO_2. These codes could take advantage of the lower pressure benchmarking problem developed by Ebigbo (2007) and used by STOMP.

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