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1 Comparison of numerical methods for 2 simulating strongly non-linear and 3 heterogeneous reactive transport problems – 4 the MoMaS benchmark case

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24 Abstract:

25 Although multicomponent reactive transport modeling is gaining wider application in various
26 geoscience fields, it continues to present significant mathematical and computational challenges.
27 There is a need to solve and compare the solutions to complex benchmark problems, using a
28 variety of codes, because such intercomparisons can reveal promising numerical solution
29 approaches and increase confidence in the application of reactive transport codes. In this
30 contribution, the results and performance of five current reactive transport codes are compared for
31 the 1D and 2D sub-problems of the so-called "Easy Test Case" of the MoMaS benchmark
32 (Carrayrou et al., this issue). As a group, the codes include iterative and non-iterative operator
33 splitting, and global implicit solution approaches. The 1D Easy Advective and 1D Easy Diffusive
34 scenarios were solved using all codes and, in general, there was good agreement, with solution
35 discrepancies limited to regions with rapid concentration changes. Computational demands were
36 typically consistent with what was expected for the various solution approaches. The most
37 important outcome of the benchmark exercise is that all codes are able to generate comparable
38 results for problems of significant complexity and computational difficulty.

1 *Keywords: MoMaS, benchmark, code intercomparison, numerical methods for*
2 *reactive transport, direct substitution approach, DSA, differential and algebraic*
3 *equations, DAE, sequential iterative approach, SIA, sequential non-iterative*
4 *approach, SNIA.*

5

6 **Introduction**

7

8 Modeling reactive transport in porous media requires the solution of a coupled set
9 of equations describing the transport of mobile chemical species together with a
10 variety of geochemical reactions (Steeffel and MacQuarrie, 1996). Since initiation
11 of research in this field, reactive transport modeling has been recognized as a
12 problem that may lead to significant mathematical and numerical difficulties.
13 These difficulties originate from numerous challenges related to the solution of
14 each operator (i.e. transport and chemistry) and the coupling of the operators used
15 to evaluate the transport and reaction phenomena. As a result, a body of literature
16 is developing that is devoted to the verification and validation of reactive transport
17 models. In addition, several authors have conducted studies focusing on the
18 performance assessment of reactive transport models and related solution
19 methods. One can distinguish between four cases for these studies:

20

- 21 • Method evaluation based on theoretical considerations.
- 22 • Comparisons of numerical results with exact or quasi-exact solutions.
- 23 • Intercomparisons of results obtained from two or more numerical methods.
- 24 • Validation of numerical models based on comparing simulation results
25 with experimental data.

26

27 A key paper based on theoretical comparisons of solution approaches was
28 presented by Yeh and Tripathi (1989). In this paper, the methods for coupling
29 transport and chemistry were studied and sequential and global methods were
30 compared with respect to memory requirements and computing time, and
31 calculations were performed based on estimates of the number of unknowns and
32 the number of operations associated with each method. The literature devoted to
33 the evaluation of errors on Transport-Chemistry (T-C) coupling follows a similar
34 approach. In several contributions (e.g. Valocchi and Malmstead 1992,

1 Kaluarachchi and Morshed, 1995, Barry et al. 1996, 1997, Leeming et al. 1998,
2 Kanney et al. 2003, Carrayrou et al. 2004), a variety of methods were evaluated
3 by comparing mass balances obtained using the sequential approaches with exact
4 mass balances.

5

6 Numerous verification studies have been performed by comparing numerical and
7 exact analytical solutions. Unfortunately, the problems handled by analytical
8 solutions are highly simplified and do not allow a full evaluation of the
9 capabilities of multicomponent reactive transport codes. Available analytical
10 solutions are typically restricted to 1D-transport of a single species in
11 homogeneous media (e.g. Van Genuchten and Wierenga, 1976; Selim and
12 Mansell, 1976; Van Genuchten 1981; Carnahan and Remer, 1984). Some studies
13 deal with 2D- and 3D-transport (Sun et al. 1999) and a few attempts have been
14 made to include more complex chemical reaction networks. For example, Toride
15 et al. (1993) considered a two-site sorption model present in both mobile and
16 immobile domains. However, analytical solutions are generally limited to
17 homogeneous and uni-directional flow fields and the geochemical system
18 involves only one or two reactions described either by isotherms or by first-order
19 rate expressions. In reality, flow systems are not restricted to one spatial
20 dimension, but may require 2D (De Windt et al. 2003) or 3D (Henderson et al.,
21 2009) spatial discretizations, often further complicated by physical and chemical
22 heterogeneities (Bauer et al., 2009) or fractures (Molinero and Samper, 2006).
23 The chemical reaction network may include instantaneous equilibrium reactions
24 (Walter et al., 1994), kinetic processes (Salvage and Yeh, 1998), or a mixed
25 reaction network (e.g. Mayer et al., 2001), subject to a high degree of coupling
26 and non-linearity. Processes may include mineral weathering and formation
27 (Maher et al., 2009), biological phenomena (Nowack et al. 2006), radioactive
28 decay (De Windt et al., 2006), competitive sorption and ion exchange (Steeffel et
29 al., 2003), isotope fractionation (Prommer et al., 2008), and may involve more
30 than 200 chemical species (e.g. Bain et al., 2001).

31

32 Model validation can be attempted by comparing numerical results with
33 experimental data. For example, Van Genuchten et al. (1977) evaluated a reactive
34 transport model based on experimental data that describes transport and non-linear

1 sorption of trichlorophenoxyacetic acid. Validation of reactive transport models is
2 an important task; however, the a priori verification of the numerical code is still
3 required because it needs to be demonstrated that the numerical code solves the
4 governing equations correctly and accurately. Comparisons of simulation results
5 to experimental data alone do not provide a suitable tool for model verification.
6 This approach does not allow distinguishing between differences that are due to
7 an incorrect implementation of the governing equations, discrepancies associated
8 with an incomplete or faulty conceptual model, or deviations associated with
9 experimental and analytical uncertainties.

10

11 Based on these limitations, a suitable avenue for model verification appears to be
12 the intercomparison of numerical results. This intercomparison involves the
13 independent solution of the same problem using a variety of models and/or
14 numerical techniques. One of the main advantages of this method is that complex
15 systems that are more representative of real world reactive transport problems can
16 be considered. The intercomparison of numerical results also has some
17 disadvantages, specifically that the "true" solution of the problem is not known;
18 however, obtaining the same or very similar results with a variety of computer
19 codes, that are based on different methods and implementations, provides
20 increased confidence in the accuracy of the codes and the field of reactive
21 transport modeling in general.

22

23 Despite these obvious benefits, very few model intercomparisons have been
24 published to date. Freedman and Ibaraki (2003) compared different solution
25 approaches to model redox processes by comparing the two codes DYNAMIX
26 and DART. De Windt et al. (2003) present an intercomparison of the reactive
27 transport codes CASTEM, CHEMTRAP, PHREEQC and HYTEC for the
28 simulation of oxidation, dissolution, and transport of uranium. The
29 intercomparison presented by De Windt et al. (2003) involves a relatively
30 complex chemistry geochemical system and a two-dimensional flow field. In
31 addition, there are very few comparisons that provide information about the
32 performance of the numerical methods used. The literature devoted to the
33 comparison of sequential and global approaches for T-C coupling (Steeffel and
34 Lasaga, 1994; Steefel and MacQuarrie, 1996; Shen and Nikolaidis, 1997; Saaltink

1 et al. 2000, 2001; Fahs et al. 2008, de Dieuleveult et al. 2009) provides some
2 discussion that is mostly qualitative in nature. Reeves and Kirkner (1988) provide
3 the computing times required for the solution of a 1D problem with sorption of
4 one, two or three components for a number of methods. In these studies,
5 comparisons are typically based on the same mesh size and/or the same time step,
6 despite the fact that each method requires its own time step and mesh size.

7
8 Hence, the literature devoted to comparison of numerical solutions for reactive
9 transport models is subject to some limitations, such as:

- 10 • low degree of complexity,
- 11 • lack of performance evaluation,
- 12 • low number (2 or 3 codes) of simultaneous comparisons.

13

14 The reactive transport benchmark of MoMaS has been designed to help filling
15 these gaps. The benchmark provides a high degree of complexity and non-linear
16 coupling, and provides a platform that allows focusing on the comparison of
17 methods and implementations by ensuring that all participants use the same
18 model. The reaction network is synthetic in nature, removing the dependence on
19 the formulation of activity corrections or database dependencies. Results are thus
20 strictly identical from a chemical perspective. The objectives of this benchmark
21 are then to compare the numerical methods and their implementations.

22 The first objective is to analyze the ability of the different methods to solve the
23 various benchmark tests. We investigate three classes of numerical coupling:
24 SNIA based on transport operator splitting and no iteration between transport and
25 chemistry; SIA, based on an implicit scheme and fixed-point iterations for
26 nonlinear coupling of transport and chemistry; global methods based on an
27 implicit scheme and Newton iterations for nonlinear coupling. We do not
28 investigate SNIA methods based on an explicit scheme.

29

30 The second objective is to provide a measure for computational efficiency.

31 Twenty years ago, Yeh and Tripathi (1989) concluded that “Those models that
32 use the DAE approach or the DSA require excessive CPU memory and CPU time.
33 They can only remain as a research tool for one-dimensional problems”. We
34 design challenging 1D and 2D test cases in order to check if nowadays, global

1 approaches can compete with sequential approaches. We compare three
2 implementations of the global approach, which differ by the number of coupled
3 unknowns, in order to measure the impact of a reduction of unknowns. The
4 efficiency is strongly related to the numerical coupling but also to the
5 discretization schemes, to the solution algorithms and to the implementation. For
6 example, various strategies have been implemented to control the time step and to
7 control the convergence of nonlinear iterations. We do not aim at ranking the
8 methods and the codes. Indeed, the conclusions are valid only for the test cases
9 used, some of the codes are still under development, and the computers used are
10 not the same. Despite of these limitations, we attempt to draw conclusions
11 regarding performance of the methods with general relevance.

12

13 The third objective is to provide a measure for the accuracy of the numerical
14 results. The comparison must be global but must also highlight some local key
15 features such as a peak of concentration. Accuracy can be analyzed qualitatively
16 by using for example visualization tools. In order to derive a quantitative measure,
17 it is necessary to define a reference solution. Again, we try to draw some general
18 conclusions, based on the results of the test cases.

19

20 This paper presents results from five different research teams using five different
21 approaches: SNIA with Operator Splitting, SIA and three variants of global
22 approaches. This contribution presents a synthesis of the results obtained by the
23 five codes. We use four test cases, from the so-called "Easy Test Case" collection
24 of the MoMaS reactive transport benchmark. Additional simulation results for
25 these test cases and other test cases (Carrayrou et al., this issue) are documented in
26 the contributions by the individual participants (de Dieuleveult and Erhel;
27 Hoffmann et al.; Carrayrou; Lagneau and van der Lee; Mayer and MacQuarrie,
28 this issue).

29

30 We first describe the reactive transport model used for designing the benchmark.
31 Then we briefly present the five codes used, along with a synthetic description of
32 their main features. Before presenting the results, we describe the methodology
33 used for achieving the objectives of comparison. Finally, we discuss the results
34 and provide some concluding remarks.

1 **Reactive transport model**

2 Reactive transport is described using the advection-dispersion equation with
3 reactions subject to the instantaneous equilibrium assumption:

$$4 \quad \omega \frac{\partial (T_{M_j} + T_{F_j})}{\partial t} = -\nabla \cdot (\omega \mathbf{u} T_{M_j}) + \nabla \cdot (\bar{\mathbf{D}} \cdot \nabla T_{M_j}) \quad (1)$$

5 | Where t is the time, \mathbf{u} is the pore [water](#) velocity, T_{M_j} is the total mobile
6 concentration for each component and T_{F_j} is the total immobile concentration. $\bar{\mathbf{D}}$
7 is the dispersion tensor and ω is the porosity. Chemical reactions give the
8 relations between T_{M_j} and T_{F_j} by the way of mass action laws and conservation
9 equations.

10

11 The chemical phenomena are summarised in form of an equilibrium tableau in
12 Table 1. The reactions involve 4 aqueous components and one immobile
13 component, leading to the formation of 5 aqueous and 2 adsorbed secondary
14 species. The characteristic of this chemical system is that it contains very high
15 stoichiometric coefficients: from -4 to 4 for component X2); and equilibrium
16 constants encompassing an extreme range from 10^{-12} for C1 to 10^{35} for C5.

17

18 A 1D and a 2D domain were studied. For both cases, the domains are
19 heterogeneous both in terms of hydrodynamic and chemical properties (see Figure
20 1). The domains are composed of 2 media: Medium A is highly permeable, with
21 low porosity and low reactivity whereas medium B has a low permeability with
22 high porosity and high reactivity. A complete description of the exercise can be
23 found in Carrayrou et al. (this issue).

24

25 **Numerical methods and codes**

26 Brief summaries of the key features of the codes used by the benchmark
27 participants are presented below with a focus on the most significant differences
28 between implementations. Table 2 provides an overview of the key characteristics
29 of the codes: The first row entries describe the method of coupling between
30 transport and chemistry operators; 2nd row entries introduce the formulation for
31 advection and dispersion operators; 3rd row entries describe the method used for

1 spatial discretisation; 4th row entries represent the time discretisation used; in the
2 5th row the method used to linearize chemical system is provided; the 6th row
3 entries describe the convergence criteria used for linearization (all criteria have
4 been tested and chosen sufficiently small to have no influence on the accuracy of
5 the proposed solutions); the last row represents the method used for the solution
6 of the linearized system of equations. For a more detailed description of the codes,
7 we refer to the individual articles in this special issue. Although this work is
8 devoted to a comparison of numerical methods implemented in the participating
9 reactive transport codes, the general capabilities of the codes are presented for
10 completeness and to provide additional perspective (Table 3).

11

12 **GDAE1D**

13 This code is based on a method of lines in combination with a global approach in
14 order to solve the partial differential algebraic equations involving transport and
15 chemistry (de Deuileveult et al., 2009; de Dieuleveult and Erhel, this issue). In the
16 current version, spatial discretization is achieved by a classical finite volume
17 method, with upwinding for advection and centered spatial discretization for
18 dispersion. The design of the mesh uses constant spatial discretization intervals.
19 The resulting differential algebraic equations (DAE) are solved by an external,
20 robust and efficient DAE solver. Time discretization is performed by a multistep
21 implicit scheme: a backward differentiation formula (BDF) with variable order
22 and variable time step. BDF is used in connection with a modified Newton
23 method in order to deal with nonlinearity. The sparse linear systems are solved by
24 a direct method, a multifrontal Gaussian elimination with pivoting. Symbolic
25 factorization and renumbering for fill-in reduction are performed once by using
26 the matrix structure. Due to the connection between BDF and Newton's method,
27 the Jacobian matrix is updated only when necessary and the time step is controlled
28 to ensure both convergence of Newton's method and the accuracy of the scheme.
29 The main computational cost is associated with the factorization of the Jacobian
30 matrix and the solution of the triangular system of equations. For large
31 computational domains, it is necessary to decrease the computational cost. Several
32 issues will be addressed in future versions: the spatial grid will be non uniform;
33 the tolerance thresholds in the DAE solver will be tuned; the substitution approach
34 will be applied in the linear system in order to reduce the number of unknowns.

1 For the benchmark exercise, 600 cells were used for the 1D advective case, while
2 400 cells were used for the 1D dispersive case. Small tolerance thresholds were
3 specified to the DAE solver.

4

5 **Code of Hoffmann et al.**

6 This solution method reduces the size of the nonlinear system and thus, the
7 required computational resources. The system of equations, consisting of PDEs
8 and ODEs for the mobile and immobile species, and nonlinear AEs describing
9 local equilibria, is transformed by (a) taking linear combinations between the
10 differential equations, (b) the introduction of a new set of variables, i.e., a linear
11 variable transformation, and (c) the elimination of some of the new variables by
12 substituting local equations, such as AEs and ODEs, into the PDEs. Application
13 of (a) and (b) leads to a decoupling of the linear PDEs; this decoupling in
14 combination with (c) leads to a reduction of the size of the nonlinear system (see
15 Kräutle et al. 2007, Hoffmann et al., this issue, and the references therein for
16 details). The system of equations is handled in the spirit of a global implicit
17 approach (one step method) and avoids operator splitting. However, the
18 substitution of the local equations does not, as is the case for other direct
19 substitution approaches, destroy the linearity of the transport term. The algorithm
20 was implemented using a software kernel for parallel computations involving
21 PDEs, called M++. M++ itself is an object oriented code based on C++. The code
22 is implemented for 2D problems and uses finite elements on unstructured grids.
23 The nonlinear system of equations is linearized using Newton's method and
24 solved using a preconditioned BiCGStab algorithm. For the solution of the flow
25 problem, mixed hybrid finite elements are used. For the flow computation in the
26 2D case of this benchmark, BDM1 (Brezzi-Douglas-Marini)-elements were used.
27 This method guarantees an accurate solution of the flow problem despite the
28 significant permeability contrast between the two media. To facilitate fair
29 comparison with the other models, the code was run on a single processor.

30

31 **SPECY**

32 SPECY uses a non-iterative operator splitting scheme for T-C coupling and for
33 advection and dispersion (Carrayrou et al. 2003). Each operator is solved

1 independently using specifically tailored methods: advection is solved using
2 discontinuous finite elements (Siegel et al. 1997), dispersion is tackled with mixed
3 hybrid finite elements; and equilibrium chemistry is solved using a combined
4 algorithm based on the Newton-Raphson technique and the Positive Continuous
5 Fraction method (Carrayrou et al. 2002). The key feature of this code is the use of
6 specific methods to solve each part of the reactive transport equation. Solving the
7 advective part using discontinuous finite elements provides an excellent
8 description of very sharp fronts and eliminates numerical diffusion and non-
9 physical oscillations. Solving the dispersion term with mixed hybrid finite
10 elements provides an exact mass balance for each element of the mesh and allows
11 the use of a non-diagonal dispersion tensor. The algorithm developed for solving
12 the equilibrium chemistry ensures the convergence of the method for all cases and
13 provides fast convergence for most cases. To optimize computational
14 performance, we used the largest time step allowed by SPECY. This constant time
15 step length is determined by a Courant-Friedrich-Levy stability criterion equal to
16 one. The reader is referred to Carrayrou (this issue) for additional details on the
17 code formulation and its application to the MoMaS reactive transport benchmark.
18

19 **HYTEC**

20 HYTEC is a reactive transport model that integrates a wide variety of features and
21 options that have evolved, after more than a decade of development, to a widely
22 used and versatile simulation tool (van der Lee et al., 2003). Solution capabilities
23 for bio-geo-chemistry are provided by the code CHESS (<http://chess.ensmp.fr>).
24 The model accounts for many commonly encountered processes including
25 interface reactions (surface complexation with electrostatic correction and cation
26 exchange), precipitation and dissolution of solid phases (minerals, colloids),
27 organic complexation, redox and microbial reactions, etc. All reactions can be
28 modeled using a full equilibrium, a full kinetic, or a mixed equilibrium-kinetic
29 approach. Thermodynamic data is taken from the database developed by the
30 Common Thermodynamic Database Project (CTDP).

31

32 The hydrodynamic module of HYTEC is adapted for hydrodynamic conditions
33 commonly encountered in the laboratory or in the field. The code allows for
34 unsaturated media, variable boundary conditions, sinks and sources (van der Lee

1 and Lagneau, 2004). HYTEC searches for an accurate solution to the multi-
2 component transport problem using an iterative, sequential, so-called strong
3 coupling scheme. Strong coupling permits variable hydrodynamic parameters as a
4 function of the local chemistry. For example, the porosity of a porous medium
5 reduces after massive precipitation of newly formed mineral phases, which
6 modifies the water flow paths and transport parameters, e.g. diffusion coefficients:
7 HYTEC solves this interdependency accurately, which makes the tool particularly
8 useful for e.g. cement alteration at long timescales (e.g. storage of wastes and
9 performance assessment).

10

11 Application domains of HYTEC are numerous and include soil pollution, acid
12 mine drainage, in situ leaching of copper or uranium, radioactive waste disposal
13 (performance assessment, near- and far field processes) and storage of greenhouse
14 gases. Other applications concern the evolution and degradation of (geo)materials
15 such as ashes, concrete, and cements; the latter often being simulated by a typical
16 CEM-I cement but more sophisticated models for cements can be used including
17 sorption on primary or secondary CSH phases, carbonation, and sulfatation of the
18 material. The strong coupling approach as outlined above make HYTEC
19 particularly useful for the modeling of long-term leaching of solidified wastes.

20

21 Efforts to develop, test and validate the HYTEC model largely exceed the scope
22 of a single laboratory and the timescale of a Ph.D. thesis. The Reactive Transport
23 Consortium (PGT or 'Pôle Géochimie-Transport', <http://pgt.ensmp.fr>) is a national
24 research project with the objective of creating a long-term framework for the
25 development of reactive transport models, reference studies and new application
26 domains. Already operational for several years, the collaborative efforts within the
27 PGT allowed to make considerable progress in the domain of reactive transport
28 modeling.

29

30 **MIN3P**

31 MIN3P is designed to simulate general flow and reactive transport problems in
32 variably saturated media for one- to three-dimensional systems. The flow solution
33 is based on Richard's equation and transport of solute is simulated using the
34 advection–dispersion equation (Mayer et al., 2002). Gas transport is by diffusion

1 only in the standard version of the code (Mayer et al., 2002) or by advection and
2 diffusion within the framework of the Dusty Gas Model (Molins and Mayer,
3 2007). Geochemical processes included are aqueous complexation, mineral
4 dissolution-precipitation, intra-aqueous kinetic reactions, gas dissolution, ion
5 exchange, surface complexation, and linear sorption. All reactions considered in
6 the simulations can be specified through a database. The code has been used for a
7 wide range of applications in the field of contaminant transport (e.g. Mayer et al.,
8 2001) and groundwater remediation (e.g. Mayer et al., 2006). The code was also
9 used for investigation of redox stability in crystalline rock formations that may be
10 considered for deep geologic repositories for nuclear waste (Spiessl et al., 2008).

11
12 The solution of the governing equations is based on the global implicit method
13 (GIM), in which the reaction equations are directly substituted into the transport
14 equations; known as the direct substitution approach (DSA) (Yeh and Tripathi
15 1989). Spatial discretization is performed using a control volume method with
16 half-cells on the boundary. The code uses implicit time weighting and provides a
17 choice of various spatial weighting schemes for advective transport, including
18 upstream weighting, which was used for the current simulations. The governing
19 equations are linearized using a modified Newton's method with variable time
20 stepping; a sparse iterative solver is used for the solution of the linearized matrix
21 equations (see Mayer and MacQuarrie, this issue, for additional details). For the
22 "Easy Test Case" presented here, the code was used without any modifications.

23

24 **Methodology of comparison**

25 In order to interest as many research teams as possible and to extend the
26 applicability of the benchmark to a wide variety of methods, the hydrodynamic
27 flow system has been kept straightforward, with only 2 media and a simple 1D or
28 2D geometry. For the same reason, the chemical system has been simplified in the
29 sense that activity corrections have been neglected and that sorption reactions do
30 not include electrostatic correction terms. On the other hand, the benchmark has
31 been designed to ensure a high degree of numerical difficulty: physical and
32 chemical heterogeneities are significant, chemical phenomena are strongly

1 coupled and nonlinear, and concentration gradients induced by external forcing
2 due to changes in boundary conditions are substantial.
3 In this contribution, we focus on a comparison of the results for the "Easy Test
4 Case", both for 1D and 2D computational domains, and for the advective and
5 dispersive scenarios. All the five codes have results for the 1D test cases; on the
6 other hand, only three codes give results for the 2D advective test case and only
7 two codes for the 2D dispersive test case; similar results for the 2D test cases can
8 also be found in de Dieuleveult's Ph-D thesis (de Dieuleveult 2008).

9
10 We first measure the computational complexity of the codes; since most of them
11 use an adaptive timestep, we only measure the CPU time in function of the
12 number of cells. The CPU time is specified in terms of a system independent CPU
13 unit, which is defined in the paper introducing the benchmark exercise (Carrayrou
14 et al., this issue). Although the CPU time comparison is intended to provide an
15 objective performance-based measure of model and method applicability for the
16 various test cases, this method has some limitations. Some codes are in the
17 process of development (GDAE1D de Dieuleveult and Erhel; Hoffmann et al.,
18 this issue) and only include a limited chemical reaction network, whereas other
19 programs (SPECY; HYTEC; MIN3P) can handle general and complex reaction
20 networks; in these codes, chemistry can be specified from a database, greatly
21 increasing model flexibility, but also generating computational overhead (see
22 Table 3). In addition, providing a measure of the computational effort independent
23 of computing hardware and compiler software is quite difficult. The
24 computational complexity must therefore be considered qualitative. For further
25 information on the variability of CPU-times as a function of system parameters
26 we refer to the contribution of de Dieuleveult and Erhel (this issue).

27
28 In the following, the accuracy of the codes is compared. Since the methods used
29 are different, they require different spatial and temporal discretizations to obtain a
30 solution of the same accuracy. Therefore, CPU as a function of grid size should
31 not be assessed in isolation. We could compare the accuracy of codes by using the
32 same number of cells in all of them. We choose a different strategy, and compare
33 the accuracy of codes by using the same normalized CPU time for all of them.
34 Maximum allowed computing times are specified for each test case investigated.

1 For the "Easy Test Case" presented here, the following maximum CPU units were
 2 imposed: 3,500 units for 1D advective case; 2,000 units for 1D dispersive case;
 3 10,000 units for 2D advective case, and 10,000 units for 2D dispersive case.
 4 Again, this exercise has some limits, but it provides some useful information.

5
 6 Since the benchmark is designed for handling complex models, there is no
 7 analytical reference solution. Since the test cases are synthetic, there is no
 8 experimental reference solution. Therefore, it is difficult to derive a quantitative
 9 comparison. For the 1D test cases, reference solutions are calculated using fine
 10 grids and small time steps, providing a basis for accuracy measurement. An
 11 example of this approach is given by Carrayrou (this issue). The validity of these
 12 reference solutions has been controlled by successive mesh and time step
 13 refinements and by comparison with refined solution from the other codes. Then,
 14 we use the reference solution to define an error criteria based on a L2 norm. The
 15 norm (L2) is calculated for the studied species ($C_{\text{calculated}}$) over the interval (noted
 16 L), which can be either the space domain (x varying from 0.0 to 2.1 in 1D case; x
 17 varying from 0.0 to 2.1 and y varying from 0.0 to 1.0 in 2D case) or the
 18 simulation time (time form 0.0 to 6,000.0). A relative error or deviation between
 19 the solutions can be quantified by the L2 norm which is defined by equation 2:

$$20 \quad L2 = \sqrt{L \times \sum_{\text{All the } L \text{ discretisation}} \left[\frac{\Delta L_i}{L} \left(C_{i,\text{calculated}} - \sum_{\substack{\Delta L_i \text{ discretisation} \\ \text{on reference}}} \frac{dL_{j,\text{ref}} \times C_{j,\text{reference}}}{\Delta L_i} \right)^2 \right]} \quad (2)$$

21 In equation 2, ΔL is the discretisation used by the calculated solution [and \$dL_{j,\text{ref}}\$ is](#)
 22 [the discretisation used by the reference solution over \$\Delta L_i\$.](#)

23
 24 For the 2D test cases, it was not possible to define a reliable reference solution
 25 because computational requirements were too high for a very refined mesh. In
 26 order to compute a L2 norm, we used the most refined computation as reference.

27
 28 This criterion gives a global quantitative comparison of accuracy. However, since
 29 there are many species, with concentrations varying in space and time, it is
 30 difficult to represent and to analyze all the results. The global quantitative
 31 comparison gives some information but does not highlight some local key points.
 32 In order to compare the local accuracy of the codes, we select representative

1 results that focus on key difficulties of the benchmark and, at the same time,
2 highlight the most significant differences between the five codes. Thus we
3 compare the results given by the codes for some specific species at some specific
4 time or location. The meaning of this comparison is to analyze if a code can
5 compute an accurate solution for a specific pollutant or near a pumping well.
6

7 **Results**

8 **Computational complexity**

9 To illustrate the computational complexity of the various codes, we plot the
10 normalised CPU times as a function of the number of cells in the mesh. Results
11 for the 1D advective and dispersive test cases are presented in Figure 2 and Figure
12 3, respectively. Results for the 2D advective test case are presented in Figure 4.
13

14 As expected, the computational complexity of all codes is characterized by a
15 linear log-log relationship between CPU-time and mesh size, independent of the
16 test case considered. It appears that all codes have the same slope for the 1D test
17 cases (except HYTEC for the 1D advective test case). For the 1D advective and
18 dispersive test cases (Figure 2 and 3), well known results are confirmed: the SNIA
19 (SPECY) is faster than other methods, for a fixed number of cells. However, as
20 suggested by Saaltink et al. (2000), implementations of the DSA approach (e.g.
21 MIN3P, Hoffmann et al.) can lead to competitive CPU performance. The new
22 reduction scheme developed by Kräutle et al. 2007 (see also Hoffmann et al., this
23 issue) decreases further the computational complexity. Despite the use of a global
24 approach, this implementation shows equivalent or lower CPU times than
25 required by all other codes. Moreover, it must be underlined that this code uses a
26 2D discretization to emulate a 1D domain. This method is more CPU-time
27 consuming than solving a 1D problem. Global methods appear very competitive
28 for the 2D advective test case. Extrapolating the performance data for each of the
29 three codes in Figure 4 shows that for a mesh with the same number of cells, the
30 CPU requirements for the code by Hoffmann et al. is more than five times lower
31 than the CPU times of the two other codes.
32

1 However, we emphasize that this measure does not provide insight for accuracy.
2 So now we present a comparison of accuracy, with all the codes using
3 approximately the same normalized CPU-time.

4 **Accuracy for 1D Easy Advective Test Case**

5 The requirement to limit CPU-times to no more than 3,500 CPU units, led to a
6 range of spatial discretizations for the various codes. GDAE1D used 600 uniform
7 cells, while HYTEC was run with 1,073 uniform cells. The SPECY and MIN3P
8 simulations were conducted with non-uniform grids. The discretization in the low
9 permeability zone in the center of the domain (Medium B) was refined by a factor
10 of 2; SPECY and MIN3P employed 6,400 and 1,760 cells, respectively.

11 Hoffmann et al. used a 2D discretization to emulate the 1D problem by replacing
12 the 1D computational domain with a narrow 2D domain. A preadapted triangular
13 mesh was used with different grid sizes in the two media: grid size h_1 in Medium
14 A and grid size h_2 in Medium B with $h_1 = 4 h_2$. The resulting mesh consists of
15 6,942 cells with 1,155 nodes in the x-direction. In Medium A, the mesh has 3
16 nodes in the y-direction.

17

18 A global quantitative comparison between the results given by each code and the
19 reference solution is performed using the L2 error norm (see Table 5). The
20 reference solution is given by SPECY using a 8,200 cells mesh and a constant
21 time step of $1.14 \cdot 10^{-4}$. All the codes provide similar error norms. The best results
22 are obtained by GDAE1D, although the approach chosen by GDAE1D is
23 computationally intensive and requires using a coarse grid to respect the specified
24 CPU time criteria. The results provided by HYTEC leads to the second L2 norm.
25 The results given by the code of Hoffmann et al. and by MIN3P lead to the 3rd and
26 4th L2 norm.

27

28 This global criterion is not sufficient to compare accuracy. To compare local
29 results for this test case, we have selected the concentration profile of the fixed
30 component S at time 10. This profile is characterized by sharp concentration
31 fronts with a very narrow peak located near the inlet of the domain (Figure 3).
32 This concentration peak is due to the disequilibrium created by the injection of
33 species X3. The influence of the more reactive medium B can be seen in the
34 centre of the domain, as indicated by the higher concentration of S. All codes

1 produce very similar concentration profiles at the scale of the solution domain.
2 More comprehensive results presented in the individual contributions for each
3 code (de Dieuleveult and Erhel; Hoffmann et al.; Carrayrou; Lagneau and van der
4 Lee; Mayer and MacQuarrie, this issue) confirm the good agreement for other
5 chemical species.
6 However, Figure 3 also reveals small discrepancies for the concentration peak
7 near the domain inlet. Zooming into this region provides a sensitive measure for a
8 more in-depth code comparison. The location and intensity of the peak at $x = 0.02$
9 (Figure 4) provide a direct indication of coupling error or numerical diffusion.
10 Figure 4 indicates that there are indeed small differences in the location of the
11 concentration peak and the magnitude of the peak concentration.
12 Table 4 provides a quantitative assessment of these differences suggesting that all
13 codes produce similar peak locations with a low standard deviation; however, the
14 maximum concentrations calculated by the various codes are characterized by a
15 wider range. Successive mesh and/or time step refinements performed using the
16 various models indicate that for the exact solution of S, the peak concentration
17 will exceed 0.9 (see Carrayrou, this issue). The reference solution is a peak of
18 0.985.
19 Even if the intensity of the peak is low with HYTEC, its localization is good and
20 the rest of the curve fits well the reference. Traditionally, one of the main
21 advantages of operator splitting methods is that tailored numerical methods can be
22 used for each operator, including exact transport schemes to minimize numerical
23 diffusion (Steeffel and MacQuarrie, 1996). This is confirmed by the results
24 obtained using SPECY (Figure 4, Table 4). However, this peak is shifted to the
25 left. Moreover, the curve between $x = 0.04$ and $x = 0.15$ is far from the reference.
26 The closest peak location and intensity to the reference is computed by GDAE1D.
27 Thus, this global method achieves high peak concentrations despite a relatively
28 coarse discretization. This is probably due to a small error tolerance in the DAE
29 solver, inducing small time steps. It seems to indicate that global methods can be
30 implemented with a low degree of numerical diffusion. For GDAE1D, some
31 differences can be seen on Figure 4 between $x = 0.04$ and $x = 0.15$, they are
32 probably due to a small number of grid cells.
33

1 **Accuracy for 1D Easy Dispersive Test Case**

2 For the 1D Easy Dispersive Test Case, the maximum normalized CPU time was
3 set to 2,000 CPU units. To meet this criterion, GDAE1D used a uniform
4 discretization with 400 cells, while the HYTEC-simulation employed 137 uniform
5 cells. As for the 1D Advective Case, the SPECY and MIN3P simulations used a
6 non-uniform discretization with grid refinement in Medium B (by a factor of 2).
7 For the SPECY simulation, the domain is discretized into 5,800 cells, while the
8 MIN3P-simulation was based on a grid with 880 cells. Hoffmann et al. used a
9 narrow 2D computational domain to describe the 1D system. However, unlike the
10 1D Advective Case, no grid refinement was performed and a regular mesh with 3
11 nodes in the y-direction was specified. The resulting grid consists of 2,184
12 triangles with 547 nodes in the x-direction.

13
14 L2 error norms are given on Table 5. The reference solution is given by MIN3P
15 using a 1,760 cells mesh and a time step limited to $CFL = 1$. Again, all codes
16 provide similar norms. Code MIN3P leads to the smallest L2 norm, followed by
17 GDAE1D, then the code Hoffmann et al., finally SPECY and HYTEC. Global
18 approaches are efficient for dispersive problems and the mesh used by MIN3P is
19 the finest among other global codes.

20
21 For this case, local accuracy measurement is based on breakthrough curves for
22 species C2 at the outflow of the domain (Figure 10). C2 concentrations increases
23 rapidly after approximately 300 time units and it equals the composition of the
24 injected solution, followed by a sharp drop due to the change of the inflow
25 boundary condition (after 5,000 time units). The simulation results indicate that
26 all codes consistently reproduce the increase and decrease of the C2 concentration
27 front (Figure 10).

28 This dispersive test case provides a serious test for implementations based on the
29 sequential approach. The short time scale of dispersive transport effectively leads
30 to an increased solute flux with possible feedback on local chemistry from several
31 neighbouring cells. These types of problems are known to be prone to the
32 introduction of coupling errors, while global methods are expected to perform
33 well.

34 This hypothesis is confirmed by the results shown in Figure 10, which indicate an
35 excellent agreement between the different global approaches (GDAE1D,

1 Hoffmann et al. and MIN3P). Discrepancies between these three codes are
2 particularly small. On the other hand, the SIA and SNIA solutions show slight
3 deviations. Minor differences are visible for the codes using the SIA and SNIA
4 methods during the flushing period ($> 5,000$ time units); however, it must be
5 emphasized that the time frame displayed is less than 5 time units, while the total
6 simulation period is 6,000 time units.

7
8 However, solutions obtained for refined grids (e.g. SPECY, Carrayrou, this issue)
9 converge towards the results obtained by the global methods, suggesting that
10 errors are reduced by refining space and time.

11

12 **Accuracy for the 2D Easy Advective Test Case**

13 The 2D version of the Easy Advective Test Case was solved using three of the
14 codes (HYTEC, MIN3P and Hoffman et al.). Again, restricting the CPU time to a
15 maximum of 10,000 units led to different spatial discretizations. Hoffmann et al.
16 used a preadapted mesh with 38,016 triangles, refined in the fast velocity zone
17 and near the outflow. The HYTEC solution used a grid with 8,840 cells (136 x 65)
18 to comply with the CPU criterion. MIN3P employed a grid with 5,250 control
19 volumes (105 x 50).

20

21 The concentration contours of component X3 at time 1,000 offer a suitable means
22 for comparison. Figure 6 clearly depicts high concentrations in the vicinity of the
23 two injection zones, one located on the left boundary and the second located near
24 the top of the model domain. High concentration regions are delineated by sharp
25 fronts controlled by sorption and complexation reactions. In addition, the
26 concentration distributions are significantly affected by the presence of Medium
27 B, which induces a deviation of the flow lines and a low concentration zone near
28 the bottom of the domain.

29

30 Comparing the results demonstrates that all codes are capable of reproducing the
31 key features of the problem (Figure 6). Overall, simulation results are similar in
32 terms of the magnitude of concentrations and the location of fronts. The most
33 significant differences are observed in the region of divergent flow downgradient
34 of the low permeability zone (Medium B) near the top of the domain (Figure 6).

1 In addition, some deviations are observed in the low concentration zone within
2 Medium B near the bottom of the domain.

3
4 In addition to the solutions computed subject to the CPU time limitation, the
5 participants could also submit solutions using finer meshes without CPU time
6 limitations. In this exercise, Hoffmann et al. used a regular mesh with 107,520
7 triangles and MIN3P was run with a grid consisting of 21,836 cells (212 x 103).
8 Figure 7 shows the X3 concentration maps at time 1,000 calculated using these
9 refined meshes. [Also, Hoffmann et al. performed a computationally intensive](#)
10 [simulation with a 608,256 cells grid, taking 2 weeks on ten processors. The mesh](#)
11 [is very fine and the unstructured mesh used is adapted to describe the meandering](#)
12 [flow field. We provide the X3 concentration map at time 1,000 for this very fine](#)
13 [mesh in Figure 8. The results of the refined simulations show that the grid](#)
14 [refinement leads to somewhat sharper concentration fronts and a reduction of](#)
15 [local oscillations \(Figure 6, Figure 7 and Figure 8\).](#)
16 [However, a more detailed analysis of this aspect was not possible due to the](#)
17 [substantial CPU-requirements associated with very fine discretizations. Only the](#)
18 [code of Hoffmann et al. was able to compute a solution on such a fine mesh.](#)
19 [Hence it was not possible to check this solution with help of a second code. For](#)
20 [this reason, we cannot conclude whether or not the three codes will converge to](#)
21 [the same solution and we do not give an error norm because we did not get a](#)
22 [reference solution.](#)

24 **2D Easy Dispersive Test Case**

25 The maximum allowed computing time for this case was set to 10,000 CPU units.
26 This benchmark was only completed by two codes. The HYTEC-simulation used
27 840 cells (42 x 20), and MIN3P employed a grid with 5,250 cells (105 x 50), the
28 same discretization as for the 2D Advective Case.

29
30 The results are compared based on the concentration contour map of the immobile
31 component S at time 10 (Figure 11). S concentrations are depleted completely in
32 the vicinity of the two injection locations and a very thin and high amplitude S
33 peak appears, similar to the results presented in Figure 3 and Figure 4 for the 1D
34 Easy Advective Test Case. The simulation results from both codes indicate that

1 these narrow and sharp peaks are difficult to resolve in a 2D simulation. A
2 possible remedy would be grid refinement; however, this is difficult to achieve
3 considering the extreme stiffness and high computational demand of this test
4 problem. Nevertheless, the results are encouraging in the sense that both
5 simulations produce the same characteristic system behaviour.

6

7 **Synthesis of results**

8 **About the benchmark**

9 The staged design of the benchmark was useful because it allowed comparing
10 numerous methods and codes, independent of the level of development. Some of
11 the established codes were able to tackle the benchmark on all three levels, while
12 codes with a more limited reaction network could also participate. Using a
13 fictitious chemical reaction network helped to focus on numerical issues and
14 ensured that differences in the results are due to methods, algorithms or
15 implementations, and not to discrepancies in the geochemistry databases. [About
16 the 2D cases, codes with parallel capabilities are needed to solve the problem
17 accurately, i.e. to define a reference solution. Another possibility for future
18 evaluation would be to make the problem "chemically easier" to allow for a
19 quantitative comparison.](#)

20 **A good confidence in all methods**

21 One of the main outcomes of this benchmark exercise is that the various methods
22 used in this paper for solving reactive transport equations were able to solve the
23 benchmark test cases and to capture their characteristic features both in time and
24 space. Despite some localized differences, the simulation results are quite
25 comparable, which builds confidence in the reactive transport numerical
26 modelling approach in general. Another outcome of this exercise is that some of
27 the codes presented here have been improved to perform this benchmark.

28 **About sequential approaches**

29 Sequential approaches for reactive transport coupling are attractive because of
30 their highest modularity and flexibility. Since models are becoming increasingly
31 more complex, a modular and "library-based" approach, in which all libraries can

1 be tested as independent modules, is strongly recommended (e.g. as implemented
2 in HYTEC). The sequential approach allows for code development by a team of
3 programmers working relatively independently. Indeed, this method breaks down
4 the reactive transport problem naturally into three major modules: chemistry,
5 transport, and coupling. Moreover, they allow the use of any chemistry solver
6 with all the knowledge of geochemistry databases. On the other hand, global
7 methods require computing chemistry functions and derivatives and cannot use
8 current chemistry solvers, which do not provide these interfaces. It is well known
9 that operator splitting combined with a non iterative sequential approach (e.g.
10 SPECY) introduces an a priori unknown error. This benchmark illustrates clearly
11 that this method can be used with a rigorous control of errors.

12

13 **About global methods**

14 We show with our results that current global approaches can handle large systems
15 describing 1D and 2D reactive transport. As a matter of fact, the simulations of
16 the 2D benchmark were not limited by system memory, but by computational
17 time. For the test cases considered, global methods are very competitive in terms
18 of computational efficiency, compared to sequential approaches.

19 We compared three codes implementing a global approach and using different
20 primary unknowns. Because GDAE1D is based on a differential and algebraic
21 system, it leads to the highest number of coupled unknowns (number of species
22 plus number of components) per number of cells. In a Direct Substitution
23 Approach like in MIN3P, the number of coupled unknowns is reduced to number
24 of components per number of cells. By the reduction scheme implemented, the
25 code of Hoffmann et al. uses even less coupled unknowns, reducing down to 3
26 decoupled components per number of cells plus 2 coupled components per
27 number of cells. A comparison of the CPU time curves (Figure 2, Figure 5 and
28 Figure 9) illustrates the interest of reducing the number of unknowns. A new
29 version of GDAE1D is under development, where a Substitution Approach is
30 applied at the linear level. This allows keeping the nice features of DAE solvers
31 with an adaptive time step based on error estimation and an adaptive control of
32 convergence for nonlinear iterations.

1 **Impact of the dominant transport phenomenon**

2 We show here that all the numerical methods are able to give an accurate solution
3 for both advective and dispersive case. Nevertheless, it seems that SNIA method
4 is well adapted for advective problems, with a good tradeoff between accuracy,
5 computational time and ease of implementation. On the other hand, using a SNIA
6 approach for a dispersive problem must be associated with an increase of the
7 computing cost by reducing the time step or by refining the mesh. SIA and Global
8 approaches are less dependent on the dominant transport phenomenon leading to a
9 good accuracy for both advective and dispersive flow. This accuracy is obtained at
10 the cost of the CPU-time for SIA approaches and at the cost of the ease of
11 implementation for Global approaches.

12

13 **About mesh and time refinement**

14 Looking Table 2, SPECY is the only code that does not use any adaptive time
15 step. Computing time is lost to perform small time steps during the steady state
16 period (time between 3,000 and 5,000). An adaptive time step is a very important
17 point to increase the efficiency of a reactive transport code without any loss of
18 accuracy. Nevertheless, all codes compared here use some heuristic methods for
19 time step adaptation based on the convergence rate of the linearization method.
20 Only GDAE1D uses an adaptive order for time discretisation and uses an error
21 estimation computed in the DAE solver. This last feature can explain its high
22 accuracy despite the coarse grids used. Further research on reactive transport
23 codes should deal with adaptive time step strategies based on a predictor-corrector
24 scheme or on error estimators.

25 Looking again Table 2, some codes use a uniform grid whereas some other codes
26 refine the mesh in medium B. This mesh refinement reduces significantly
27 computational time. None of the code uses adaptive mesh refinement. This is also
28 a main perspective of research for reactive transport codes.

29 **Conclusion and future work**

30 A new benchmark has been designed to compare numerical methods for reactive
31 transport models. This paper presents four different test cases, in 1D and 2D, with
32 advective or dispersive transport conditions. Three classical methods for coupling

1 have been used to solve this benchmark: SNIA with Operator Splitting (SPECY);
2 SIA (HYTEC), DSA (MIN3P). In addition, two new mathematical methods have
3 been proposed for the solution of reactive transport problems: a DAE approach
4 (GDAE1D) and a reduction scheme (code of Hoffmann et al.). The use of a DAE
5 solver provides an easy way to adapt the time step and to control convergence of
6 Newton iterations, leading to accurate solutions. The reduction scheme presents
7 an important innovation for this field of research, since it allows obtaining
8 accurate solutions at a relatively low computational cost. Implementation of this
9 reduction scheme may also benefit other approaches. In the case of iterative fixed-
10 point approaches, it could be a way of reducing the number of Picard iterations
11 between chemistry and transport. In the case of non iterative approaches, the
12 reduction method may help to control errors. These two points could be targets for
13 future research.

14 The most important outcome of this benchmark exercise is that all approaches
15 (SNIA, SIA, DSA, and DAE) were able to generate accurate results for problems
16 of significant complexity and computational difficulty. This finding builds
17 confidence in the use of reactive transport models to help in the assessment of
18 environmental problems in earth sciences and engineering. It has also confirmed
19 that various approaches have different advantages and disadvantages; therefore, a
20 single superior method that is best for all problems cannot be identified.

21 Nevertheless, the good performance of the relatively new code by Hoffmann et
22 al., both in terms of relative accuracy and efficiency, highlights the need for
23 continued collaboration between mathematicians, computer scientists,
24 hydrogeologists, and geochemists.

25

26 The benchmark can also be used as a starting point for new comparison exercises.
27 For example, simulations could be enhanced to address a limitation of the current
28 tests. None of the current simulations provide a thorough test for analyzing the
29 effect of transverse dispersion. This deficiency could be removed in the 2D
30 version of the benchmark simply by modifying the boundary conditions to
31 prescribe the injection of different solutions in each injection zone. Dissolved
32 species contained within these solutions would mix along the flowpath and could
33 react with each other subject to either equilibrium or kinetic reactions. In this
34 context, various scenarios could be envisioned, in which the product of the mixing

1 reaction precipitates (equilibrium, kinetically controlled), sorbs, or remains in
2 solution. In addition, the number of components and species could be increased in
3 order to be more representative of real-world reactive transport problems.
4

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1	Tables Caption
2	
3	Table 1: Equilibrium table for the easy test case.
4	
5	Table 2: Summary of the main features of the compared codes.
6	
7	Table 3: Summary of the main phenomena and models included into the compared codes.
8	
9	Table 4: Location and peak amplitude for the first S peak at time 10 for the 1D Easy Advective
10	Test Case.
11	
12	Table 5: L2 norm for the different test cases calculated versus a reference solution.

1	Figures Caption
2	
3	Figure 1: Scheme of the 1D and 2D domains
4	
5	Figure 2: Normalized computing times as a function of discretization for the 1D Easy Advective
6	Test Case
7	
8	Figure 3: Concentration profiles of solid component S at time 10 for the 1D Easy Advective Test
9	Case.
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19	
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22	
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