COMPARISON OF THE SUITABILITY OF THE GLOBAL IMPLICIT METHOD AND THE SEQUENTIAL NON-ITERATIVE APPROACH FOR MULTICOMPONENT REACTIVE TRANSPORT MODELLING

Angus I. Calderhead, INRS-ETE UQ/U Laval, Québec, Canada
K. Ulrich Mayer, Department of Earth and Ocean Sciences, UBC, Vancouver, Canada

ABSTRACT

Multicomponent reactive transport models are useful tools for testing conceptual models and quantifying coupled hydrogeological and geochemical processes found in field situations. Computational demand is an important factor that may limit the usefulness and applicability of these models. This paper focuses on the problem-specific performance assessment of two commonly used solution techniques: The “Global Implicit Method” (GIM), in which case chemical reactions and physical transport processes are solved simultaneously, and the two-step “Sequential Non-Iterative Approach” (SNIA), in which case chemical reactions and physical transport processes are solved sequentially. Three hypothetical reactive transport problems are used to evaluate the computational efficiency and accuracy of both methods. The results demonstrate that the time step in the SNIA is always limited by a Courant number less than 1 to ensure an acceptable level of accuracy. For problems where dissolved species are strongly attenuated due to heterogeneous reactions such as ion exchange or mineral dissolution-precipitation reactions, the GIM potentially allows large time steps corresponding to Courant numbers exceeding 1000 without a loss of accuracy. For these types of problems, the GIM may be significantly more efficient, while the SNIA is typically a better choice for problems where attenuation due to heterogeneous reactions does not play a significant role.

RÉSUMÉ

Les modèles de transport réactifs multicomposantes sont des outils pratiques pour tester et analyser les modèles conceptuels et quantifier les processus couplant l’hydrogéologie et la géochimie retrouvés sur le terrain. La demande de calcul est un facteur important qui peut limiter l’utilité et l’application de ces modèles. Ce papier met en évidence l’évaluation des performances liées à des problèmes spécifiques pour deux techniques de solutions communément utilisées : dans un premier cas le GIM, là où les réactions chimiques et les processus de transport physique sont résolus simultanément et dans un second temps, le SNIA dans lequel les réactions chimiques et les processus de transport physique se font de manière séquentielle. Trois problèmes de transport réactifs hypothétiques sont utilisés pour évaluer l’efficacité de calcul et l’exactitude de ces méthodes. Les résultats démontrent que le pas de temps dans le SNIA est toujours limité par un nombre de Courant inférieur à 1 pour assurer un niveau acceptable d’exactitude. Pour des problèmes dans lesquels des espèces dissoutes sont fortement atténuées suite à des réactions hétérogène telles que des échanges d’ions où des réactions en dissolution–précipitation de minéraux, le GIM peut permettre des pas de temps larges correspondant à des nombres de Courant excédant 1000 sans perte d’exactitude. Pour ces types de problèmes, le GIM peut être significativement plus efficace alors que le SNIA est typiquement un meilleur choix pour des problèmes ou l’atténuation due à des réactions hétérogènes ne jouent pas un rôle significatif.

1. INTRODUCTION

Multicomponent reactive transport modeling can be useful for investigating coupled transport and geochemical reaction processes in aquifers and as a result numerous codes have been developed in the last decade (e.g.: Steefel and Lasaga, 1994, Parkhurst et al., 1995, Lichtner, 1996, Mayer et al., 2002, Prommer et al., 2003). An important property of any numerical model is the required computation time for a given problem. Advances in computing technology over the past years have allowed solving problems significantly faster. These advances enable the modelers to tackle scenarios that would not have been considered just a few years ago due to their complexity and shear computing volume.

Various algorithms are available for the solution of reactive transport problems. These methods include:

- Global Implicit Methods (GIM)
  (Direct coupling of chemistry and transport)
    - Direct Substitution Approach (DSA)
    - Differential/Algebraic Equations Approach (DAE)
- Sequential Methods(Keep chemistry and transport apart)Sequential Iterative Approach (SIA)
    - Sequential Non-Iterative Approach (SNIA).

Yeh and Tripathi (1989) stated that “Only those models that employ the SIA can be used for realistic applications. Those models that use the DAE approach or the DSA require excessive CPU memory and time. They can only remain a research tool for one-dimensional problems.” However, later studies by Saaltink et al. (2001) showed less favourable results for sequential methods: “The SIA …. gives problems for at least two types of cases: cases with high kinetic rates and cases with a high number of flushed pore volumes. …For some problems....the DSA may be the most (if not the only) viable choice”

As recognized by Saaltink et al (2001), the computational efficiency of the various approaches appears to be not only method-dependent, but also problem-dependent. Here, we examine the differences in relative CPU times and accuracy between the Global-Implicit Method (GIM) in form of the more common DSA formulation and the widely used Sequential Non-Iterative Approach (SNIA), and then evaluate the applicability of both solution methods for certain problem classes. The objective of this paper is to compare the suitability of the GIM and the SNIA for solving reactive transport problems and classify types of applications most suitable to be solved by the different methods.

The numerical model MIN3P (Mayer et al., 2002) is used for simulating problems using the Global Implicit Approach while PHAST (Parkhurst, 1998) is used to demonstrate the use of the Sequential Non-Iterative Approach. It is not the purpose of this paper to compare the efficiency of the two codes. In order to provide a fully quantitative comparison between the solution methods, it would be necessary to implement both methods into a single code. This could be addressed in future studies. However, using MIN3P and PHAST for the simulations is a suitable approach for highlighting the performance of the different solution methods in a semi-quantitative manner.

We examine three hypothetical reactive transport scenarios: ion exchange and dedolomitization (involving homogeneous and heterogeneous reactions), and equilibrium intra-aqueous redox reactions (involving only homogeneous reactions). For all three problems, a series of simulations was conducted under variation of the Courant number (Cr = $v \cdot \Delta t/\Delta x$). For the ion exchange problem and the dedolomitization problems, the cation exchange capacity and the initial dolomite content were also varied by several orders of magnitude. Great care has been taken that all other physical and chemical model parameters were identical. Both codes used upstream spatial weighting and implicit time weighting. All simulations were run until the pore water composition at the domain outlet approached the composition of the inflowing water. Differences in the accuracy of results, CPU times, and number of time steps required were recorded.

2. SYMBOLIC DESCRIPTION OF COUPLING METHODS

Every coupling method combines the transport equations, the kinetic reaction equations, and the equilibrium reaction equations. The transport equations are linear partial differential equations, the kinetic reactions are typically non-linear partial differential equations, and the equilibrium reactions are non-linear algebraic equations. The following section gives a brief description of the two coupling approaches studied in this paper. Considering that our focus is on illustrating the coupling techniques, we have only included transport and kinetic reaction processes into the equations for ease of presentation. Both codes used in this study are also capable of including equilibrium reactions, and use of this option was made.

2.1 Sequential Non-Iterative Approach

The sequential non-iterative approach is split up into two steps, first the transport step is computed, this is followed by the reaction step. The linear partial differential equation for the transport step is as follows:

$$\frac{\partial}{\partial t}[\phi T_j^a] \underbrace{- \nabla \cdot [q_a T_j^a] + \nabla \cdot [\phi D_a \nabla T_j^a]}_{transport\ \ operator\ \ L(T_j^a)} = 0 \qquad j = 1, N_c$$

where t is time, ϕ is porosity, T_j^a is the total concentration of the aqueous components, q_a is the Darcy velocity vector, D_a is the dispersion tensor, and N_c is the number of components considered in the problem.

The reaction operator, which assumes no transport, can be described by a set of non-linear ordinary differential equations:

$$\frac{\partial[\phi T_j^a]}{\partial t} = \underbrace{Q_j^a}_{reaction\ \ operator} \qquad j = 1, N_c$$

where Q_j^a is a source and sink term due to kinetic reactions. Equilibrium reactions, described by algebraic equations, are implicitly included in the total concentration term. In the SNIA, these two sets of equations are solved sequentially during each time step without iteration. As has been investigated in a number of previous studies (Valocchi and Malmsted, 1992; Kaluarachchi and Morshed, 1995; Barry et al., 1996), this method introduces a splitting error, which can be minimized by using small time steps during the numerical solution.

2.2 Global Implicit Method

The Global implicit method solves transport and reactions simultaneously in a single step. The set of non-linear partial differential equations can be defined as:

$$\frac{\partial}{\partial t}[\phi T_j^a] \underbrace{- \nabla \cdot [q_a T_j^a] + \nabla \cdot [\phi D_a \nabla T_j^a]}_{transport\ \ operator\ \ L(T_j^a)} = \underbrace{Q_j^a}_{reaction\ \ operator} \qquad j = 1, N_c$$

Although at first glance, the GIM seems to be advantageous because it avoids the operator splitting error, concerns over excessive CPU times caused by the solution of a large non-linear set of matrix equations (Yeh and Tripathi, 1989) and ease of implementation have encouraged the development of several codes based on the SIA and SNIA approaches.

3. MODEL PARAMETERS

This section defines physical and geochemical parameters for the scenarios studied in this paper. All three reactive transport problems use the same solution domain, physical properties, and grid spacing.

3.1 Physical model parameters

The simulations were carried out in a 10 m long domain with a 10 m^2 cross sectional area. Uniform flow was assumed and the average linear groundwater flow velocity was chosen to be 1 m day^{-1}, corresponding to a residence time of 10 days in the solution domain. Although the flow field is one-dimensional, a three-dimensional grid was used to ensure that an identical number of nodes were used in all simulations. Physical and discretization parameters for the simulations are summarized in Table 1.

Table 1: Physical model parameters for example problems

Parameter	**Value**	**Unit**
Dimensions of solution domain	10.0 x 10.0 x 1.0	[m]
Porosity	0.3	[-]
Hydraulic conductivity	10.0	[m day^{-1}]
Hydraulic gradient	0.03	[-]
Longitudinal dispersivity	0.1	[m]
Δx	0.25	[m]
Δy	5.0	[m]
Δz	0.5	[m]

3.2 Hydrogeochemical model parameters

3.2.1 Ion Exchange

The first example simulates advective-dispersive transport in the presence of a cation exchanger and is loosely based on an example calculation for the program PHREEQM (Appelo and Postma, 1993, example 10.13, p. 431-434). Initially, the domain contains a sodium-potassium-nitrate solution in equilibrium with a cation exchanger (Table 2). The domain is then flushed with a calcium-chloride solution (Table 2). Calcium, potassium, and sodium react to equilibrium with the exchanger at all times. In our simulations, the cation exchange capacity (CEC) is varied over 4 orders of magnitude (Table 2) within a range that is reasonable for groundwater applications.

3.2.2 Dedolomitization

This scenario simulates the infiltration of slightly acidic water that is undersaturated with respect to calcite and dolomite into an aquifer that contains dolomite. Initially the pore water within the aquifer is in equilibrium with dolomite (Table 2). In this case, the initial dolomite content of the aquifer is varied from 0.002 vol% to 20 vol%, corresponding to a variation over 5 orders of magnitude (Table 2).

3.2.3 Equilibrium Redox Mixing

The last example describes an aquifer that initially contains oxidizing groundwater and is infiltrated by a strongly reducing groundwater containing hydrogen sulfide (H_2S) and methane (CH_4) (Table 2). Redox equilibrium is assumed for this simulation, implying that reactions will occur due to dispersive-diffusive mixing at the interface that forms when the reducing water displaces the oxidized pore water from the domain.

Table 2: Chemical model parameters for example problems

1 -- Ion Exchange			
Parameter	Inflow	Back-Ground	Unit
pH	7.0	7.0	[-]
Ca^{2+}	6.0 x 10^{-4}	1.0 x 10^{-9}	[mol L^{-1}]
Cl^-	1.2 x 10^{-3}	1.0 x 10^{-9}	[mol L^{-1}]
K^+	1.0 x 10^{-9}	2.0 x 10^{-4}	[mol L^{-1}]
Na^+	1.0 x 10^{-9}	1.0 x 10^{-3}	[mol L^{-1}]
NO_3^-	1.0 x 10^{-9}	1.2 x 10^{-3}	[mol L^{-1}]
CEC	N/A	0.0175 - 17.5	[meq $(100g)^{-1}$]
2 – Dedolomitization			
Parameter	Inflow	Back-ground	Unit
pH	3.0	7.97	[-]
CO_3^{2-}	5.5 x 10^{-3}	1.1 x 10^{-3}	[mol L^{-1}]
Ca^{2+}	4.2 x 10^{-3}	1.2 x 10^{-3}	[mol L^{-1}]
Mg^{2+}	7.1 x 10^{-5}	8.8 x 10^{-4}	[mol L^{-1}]
Na^+	9.9 x 10^{-5}	1.0 x 10^{-4}	[mol L^{-1}]
SO_4^{2-}	4.8 x 10^{-3}	8.5 x 10^{-4}	[mol L^{-1}]
Cl^-	2.4 x 10^{-4}	1.4 x 10^{-3}	[mol L^{-1}]
Initial dolomite volume fraction	N/A	0.00002 -0.2	[cm^3 dolomite cm^{-3} sediment]
3 -- Redox Mixing			
Parameter	Inflow	Back-Ground	Unit
pH	7.0	7.0	[-]
O_2 (aq)	pe = -5	pO_2 = 0.21	[-] or [atm]
CH_4 (aq)	3.0 x 10^{-4}	-	[mol L^{-1}]
CO_3^{2-}	-	1.0 x 10^{-7}	[mol L^{-1}]
SO_4^{2-}	-	1.0 x 10^{-7}	[mol L^{-1}]
HS^-	4.0 x 10^{-4}	-	[mol L^{-1}]
Na^+	2.0 x 10^{-4}	2.8 x 10^{-7}	[mol L^{-1}]

Note for Table 2: All simulations were conducted at 25^{o}C using equilibrium constants defined in the PHREEQC database (Parkhurst et al., 1999)

4. RESULTS AND DISCUSSION

The main focus of this section is to provide an analysis of the efficiency of the two solution techniques for the various example problems, while maintaining an acceptable level of accuracy. To provide a basis for this discussion, simulations were conducted using both codes with a time step of 0.025 days yielding a Courant number of Cr = 0.1. Using this small time step, both solution methods gave simulation results that were virtually identical. Subsequently simulations with larger Courant numbers were conducted for the various scenarios, while keeping track of execution times and errors introduced. Based on this information, a maximum Courant number can be defined that yields results with acceptable accuracy for each method. Based on the recorded CPU times, the efficiency, and therefore suitability of the methods for a specific problem type can be determined.

4.1 Ion Exchange:

Figure 1 presents the results for the highest ion exchange capacity of 17.5 meq 100 g^{-1} sediment. Initially the ion exchanger contains both Na-X and K-X, which is then entirely replaced by K-X and subsequently replaced by $Ca\text{-}X_2$ (Figure 1a and b). Both the GIM and the SNIA yield virtually identical results for Cr = 0.1.

Simulated potassium (K) concentrations have been used to visually assess the accuracy of the GIM (Figure 1c) and the SNIA (Figure 1d) as a function of increasing Courant numbers. The GIM shows results that are virtually identical to the base case simulation (Cr = 0.1) for Courant numbers up to 100, with some differences developing for Cr = 1000. For clarification, a Courant number of 1000 implies in this case (40 grid cells in flow direction) that the entire solution domain will be flushed 25 times during a single time step. The SNIA already starts to deviate from the base case results for a Courant number of Cr =1 and shows significant deviations for any Cr > 1. This is not entirely surprising, because large time steps introduce a significant operator splitting error, when using the SNIA (Kaluarachchi and Morshed, 1995). For practical purposes, the time steps in the SNIA have to be defined such that Cr < 1 to minimize the operator splitting error.

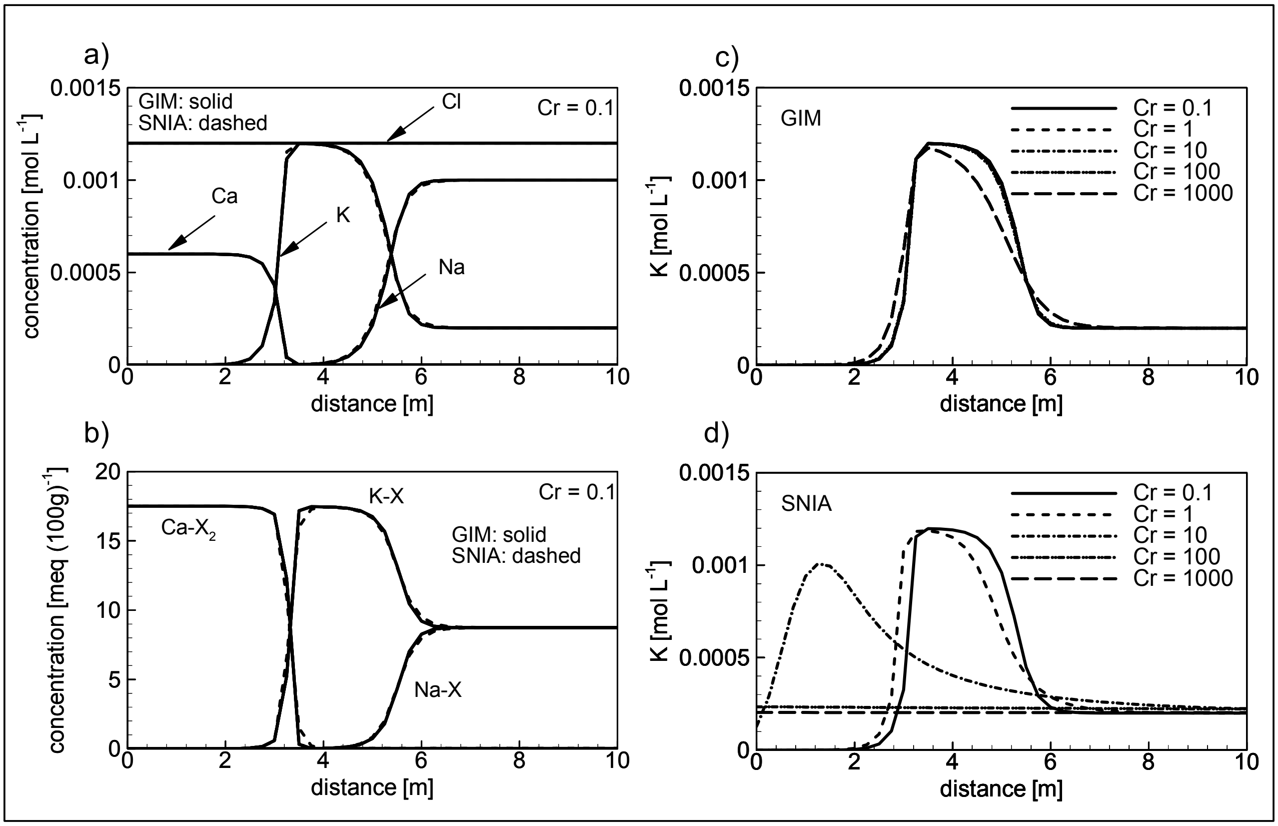

Figure 1: Simulation results for ion exchange scenario (t3000 days, CEC = 17.5 meq $(100g)^{-1}$), a) aqueous concentrations for Cr = 0.1, GIM and SNIA, b) surface species for Cr = 0.1, GIM and SNIA, c) aqueous potassium concentrations for GIM, Cr = 0.1-1000, d) aqueous potassium concentrations for SNIA, Cr = 0.1-1000

For the chosen range of time steps, the SNIA gives acceptable results for Cr = 0.1, while the GIM provides acceptable results for Cr = 100. The corresponding CPU times are 2 min 47 sec for the GIM, and 11 h 21 min 11 sec for the SNIA (Table 3). Although the MIN3P and PHAST codes are quite different in terms of the numerical techniques employed, this relatively large difference (a factor of 245), suggests that the GIM is the more efficient method for the solution of the current problem. This is primarily due to the large, but not unrealistic (Appelo and Postma, 1993), ion exchange capacity, which leads to significant effective retardation of the dissolved species. For example, after 3,000 days sodium (Na) has only been displaced from the column up to 5.5 m (for $c/c_{initial} = 0.5$) (Figure 1a), corresponding to a displacement velocity of 1.8×10^{-3} m day^{-1}. This in hand corresponds to an effective retardation (R_{eff}) value of 545. These results suggest that the GIM can provide accurate solutions, as long as the time step is defined such that $Cr < R_{eff} v\Delta t / \Delta x$, while the SNIA is limited by $Cr < v\Delta t/\Delta x$ (where v and Δx, remain constant). It needs to be clarified that R_{eff} varies for different components in multicomponent reactive transport. Typically, the smallest R_{eff} of the components of interest will control the time step, which is the one for potassium in the current example.

It is logical that R_{eff} will vary with ion exchange capacity. For small cation exchange capacities, the GIM does not allow very large time steps without jeopardizing accuracy. As a matter of fact, for very small CEC's, the maximum time step providing sufficient accuracy decreases to the same value than the one for the SNIA. In this case the SNIA is the more efficient solution method by a factor of 3.7 (Table 3).

Table 3: GIM/SNIA CPU times for ion-exchange scenario. The highlighted fields indicate the most efficient simulation while providing acceptable accuracy for both methods (all simulations were conducted using a Pentium III 700MHz Processor).

CEC [meq $(100g)^{-1}$]	Simulation time [days]	Courant number	CPU time (h:min:sec)	
			GIM	SNIA
0.0175	15	0.1	0:03:22	0:00:54
		1	0:00:29	0:00:09
		10	0:00:06	0:00:02
0.175	150	0.1	0:22:30	0:07:56
		1	0:02:56	0:01:03
		10	0:00:28	0:00:12
1.75	1,500	0.1	2:53:01	1:17:55
		1	0:21:47	0:09:39
		10	0:02:43	0:01:38
		100	0:00:27	0:00:12
17.5	15,000	0.1	23:38:25	11:21:11
		1	3:01:42	1:32:19
		10	0:21:47	0:16:48
		100	0:02:47	0:02:19
		1000	0:00:27	0:00:15

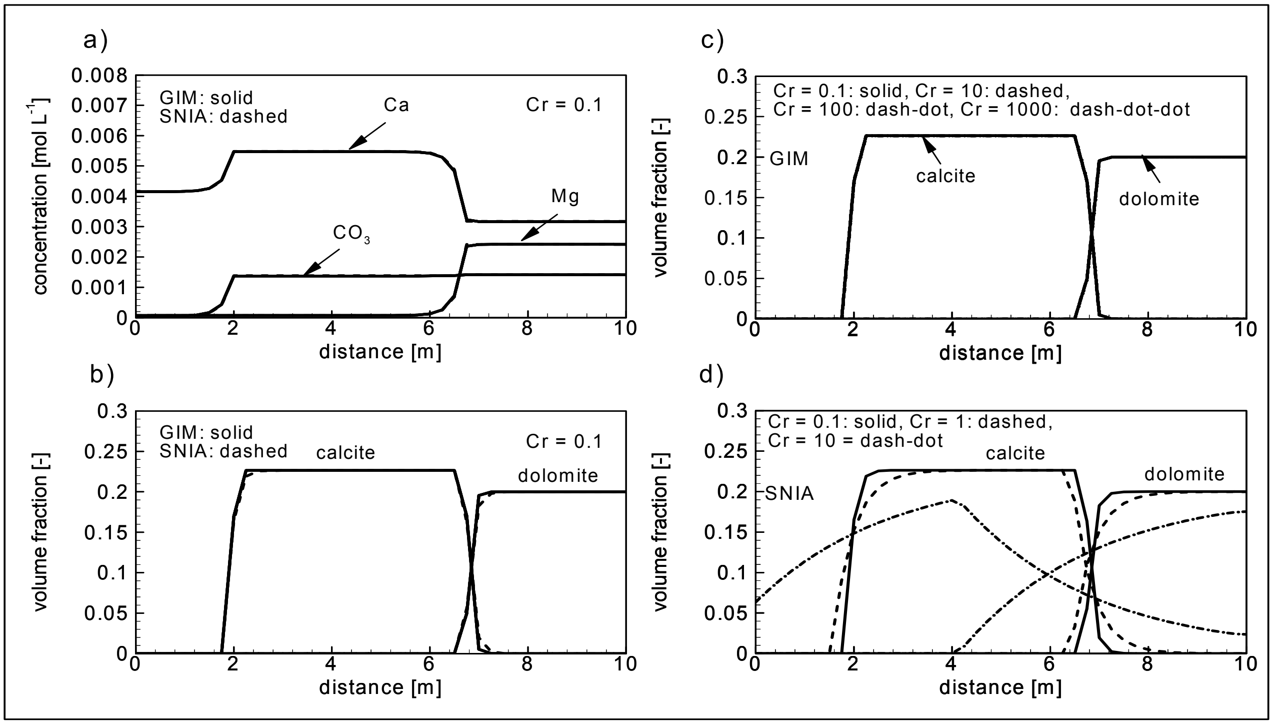

Figure 2: Simulation results for dedolomitization scenario (30,000 days, initial dolomite content 20 vol%) a) aqueous concentrations for Cr = 0.1, GIM and SNIA, b) mineral volume fractions for Cr = 0.1, GIM and SNIA, c) mineral volume fractions for GIM, Cr = 0.1-1000, d) mineral volume fractions for SNIA, Cr = 0.1-10

4.2 Dedolomitization

This simulation demonstrates the replacement of dolomite by calcite, and subsequent dissolution of calcite driven by the infiltration of slightly acidic, calcium-rich water (Figure 2 a and b). The simulation results are shown for an initial dolomite content of 20 vol%. Again, there is favorable agreement between the solutions using the GIM and SNIA for a Courant number Cr = 0.1.
For this problem, the GIM yields a solution with acceptable accuracy up to a Courant number of 1000, while the SNIA is again limited by Cr = 0.1, as can be expected. Dedolomitization is a problem that appears to be particularly well suited for the application of the GIM (see also Saaltink et al., 2001), due to the strong attenuation of dissolved components during the dedolomitization process. R_{eff} for Mg displacement is approximately 4600. This is not surprising, because dissolution-precipitation reactions have the potential to cause greater and longer lasting effects on the geochemical evolutions in aquifers than ion exchange and sorption reactions.

Table 4: GIM/SNIA CPU times for dedolomitization scenario. The highlighted fields indicate the most efficient simulation while providing acceptable accuracy for both methods (all simulations were conducted using a Pentium III 700MHz Processor). N/C : non-convergent, N/A : simulation not completed due to excessive CPU-times

Initial dolomite volume fraction	Simulation time [days]	Courant number	CPU times (h:min:sec)	
			GIM	SNIA
0.00002	25	0.1	0:06:18	0:01:35
		1	0:01:35	0:00:13
		10	0:00:17	0:00:03
0.0002	210	0.1	0:31:58	0:10:35
		1	0:05:11	0:01:23
		10	0:01:18	0:00:13
0.002	2,100	0.1	3:10:39	1:30:11
		1	0:22:20	0:10:56
		10	0:03:49	0:01:45
		100	0:01:11	0:00:23
0.02	21,000	0.1	24:51:57	16:25:16
		1	2:43:10	1:38:32
		10	0:19:42	0:16:11
		100	0:03:25	0:03:38
		1000	0:01:14	0:00:22
0.2	210,000	0.1	N/A	N/A
		1	24:41:27	16:06:18
		10	2:40:08	2:28:13
		100	0:19:30	0:33:19
		1000	0:03:28	0:03:25
		10000	N/C	0:00:12

A quantitative comparison of the efficiency of the two methods cannot be provided in this case, because the SNIA-simulation had to be terminated, considering that the completion of the simulation would have required several days. Using the GIM, the solution of the problem (Cr = 1000) required 3 min 28 sec (Table 4).

Similarly to the cation exchange problem, a decrease of the initial dolomite content of the aquifer alters the effective retardation of the aqueous components and therefore affects the conclusions about the efficiency of the methods. For very small initial dolomite volume fractions (2×10^{-3} vol %), the SNIA becomes more efficient by a factor of 4 (Table 4).

4.3 Equilibrium Redox Mixing

Unlike the previous two problems, this test example does not consider heterogeneous reactions, i.e. reactions between dissolved species and minerals or adsorbed species. All components present in the simulation are therefore unretarded. Reactions occur only in the mixing zone present between the infiltrating pore water and the pore water that is being displaced. In this case, hydrogen sulfide as well as methane are oxidized by dissolved oxygen (Figure 3 a). As for the other cases, the simulation results for the GIM and SNIA compare well for a Courant number of Cr = 0.1.

Based on the discussion of the results from the previous examples, we would expect that the SNIA is the better suited method for this type of problem, due to the lack of effective retardation. Examining Table 5 and Figure 3 confirms this hypothesis. Both methods show increasing deviations from the base case simulations with increasing time steps (Figure 3) and the SNIA is computationally significantly more efficient in any case (Table 2). The discrepancies are simply due to increased numerical dispersion. When homogeneous kinetic reactions are included, the problem becomes more complicated due to additional time step constraints in the SNIA (e.g.: Valocchi and Malmsted., 1992). However, for problems only involving homogeneous reactions (equilibrium or kinetic), the GIM will always be limited by Cr < 1 to provide sufficient accuracy. It may therefore be generally valid to conclude that the SNIA is the more efficient method for problems involving only equilibrium homogeneous reactions.

Table 5: Redox mixing scenario CPU times (10 days) The highlighted fields indicate the most efficient simulation while providing acceptable accuracy for both methods (all simulations were conducted using a Pentium III 700MHz Processor).

Courant number	CPU-time [h:m:s]	
	GIM	SNIA
0.1	0:02:21	0:00:25
1.0	0:00:53	0:00:04
10	0:00:10	0:00:02

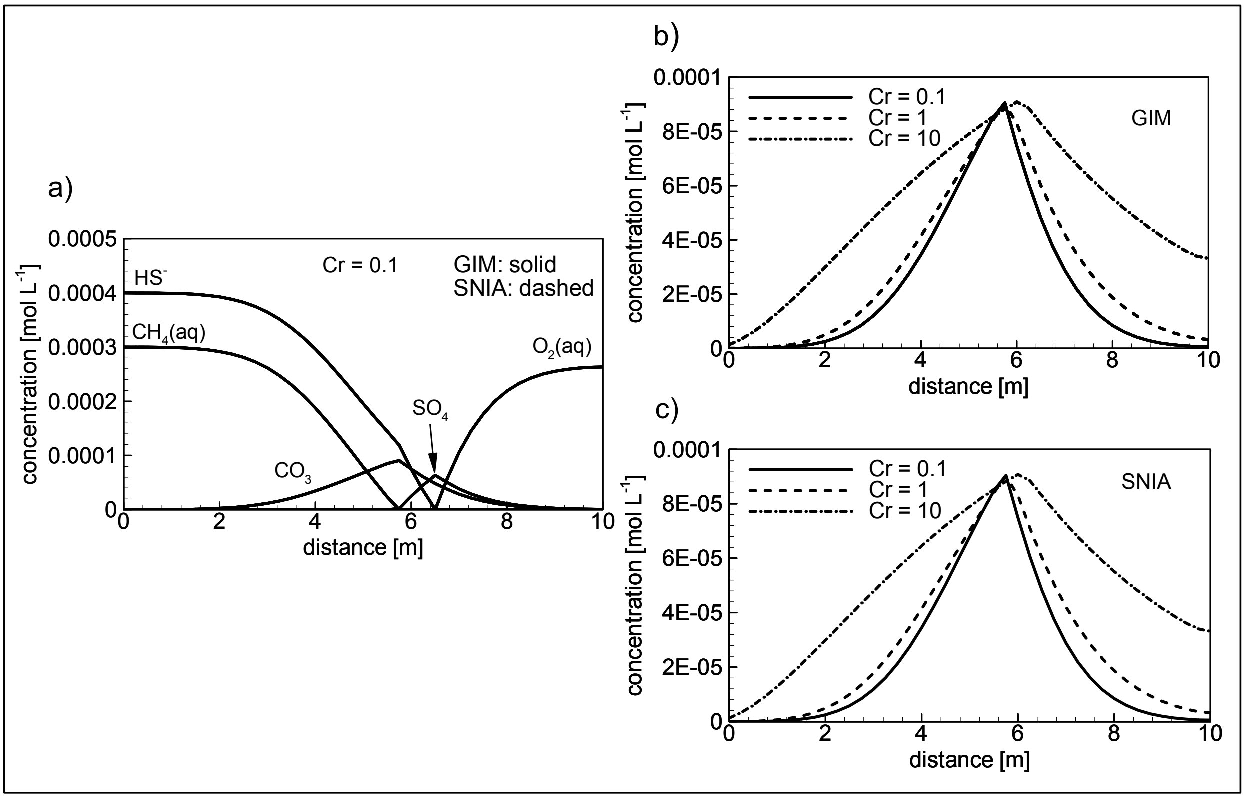

Figure 3: Simulation results for redox mixing scenario (5 days), a) aqueous concentrations for Cr = 0.1, GIM and SNIA, b) carbonate concentrations for GIM, Cr = 0.1-10, c) carbonate concentrations for SNIA, Cr = 0.1-10

5. CONCLUSIONS

The test examples investigated here have demonstrated that the GIM can be far more effective than the SNIA in solving certain classes of reactive transport problems. Reactive transport problems amenable to the solution by the GIM show a significant retardation of dissolved species, requiring a significant degree of rock-water interaction, which may be due to reactions at the solid-solution interface (sorption and ion exchange) or dissolution-precipitation reactions. The latter case has a more significant potential for attenuating the transport of dissolved species, and therefore is under certain conditions most suitable for solution by the GIM.

If rock water interaction is insignificant or non-existent, the SNIA appears to be the method of choice, because it is able to provide simulation results of comparable accuracy using less CPU time.

The results presented here need to be considered with some care, considering that two different codes (MIN3P and PHAST) have been used to conduct the simulations. However, considering the large differences in performance, the conclusions drawn here should also remain valid in a more general sense.

It also needs to be highlighted that the simulations presented here were simple scenarios. In real applications, reactive transport problems often involve a variety of processes in a more complex and heterogeneous flow field, which may dilute the differences in efficiency between the two methods.

We would like to conclude that our results indicate that both the GIM and SNIA are useful for solving reactive transport problems and that it cannot be generalized that one method is superior to another. The choice of method (and code) should take into consideration the type of reactive transport problem to be solved.

6. ACKNOWLEDGEMENTS

An NSERC (Natural Sciences and Engineering Research Council of Canada) discovery grant held by K.U. Mayer helped fund this research.

7. REFERENCES

Appelo, C. A. J. and D. J. Postma, 1993. *Geochemistry, groundwater and pollution*, A. A. Balkema, Rotterdam, Netherlands.

Kaluarachchi, J. J., and J. Morshed, 1995. Critical assessment of the operator-splitting technique in solving the advection-dispersion-reaction equation: 1. First-order reaction, *Adv. Wat. Resour.*, 18:89-100.

Lichtner, P. C., 1996a. Continuum Formulation of Multicomponent-Reactive Transport, Ch. 1 in.: *Reactive Transport in Porous Media*, Eds.: Lichtner, P. C., C. I. Steefel and E. H. Oelkers, Rev. Mineral, 34, Mineralogical Society of America, Washington, DC.

Mayer, K. U., E. O. Frind, and D. W. Blowes, 2002. Multicomponent reactive transport modeling in variably saturated media using a generalized formulation for kinetically controlled reactions, *Water Resour. Res.*, 38(9), 1174, doi: 10.1029/2001WR000862.

Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.Parkhurst, D.L., Engesgaard, P., and Kipp, K.L., 1995. Coupling the geochemical model PHREEQC with a 3D multi-component solute transport model. In *Fifth Annual V. M. Goldschmidt Conference*, Penn State University, University Park, Pennsylvania USA, May 24–-26, 1995. Geochemical Society.

Parkhurst, D.L., 1998, PHAST (Beta Version)--A Computer Program for Simulating Ground-Water Flow, Solute Transport, and Multicomponent Geochemical Reactions Ground-Water Flow and Multicomponent Geochemical Reactions, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast

Prommer, H, D. A. Barry, and C. Zheng, 2003. MODFLOW/MT3DMS based reactive multi-component transport model. *Ground Water*, 42: 247-257.

Saaltink, M.W., J. Carrera, and C. Ayora, 2001. On the behavior of approaches to simulate reactive transport. *J. Contam. Hydrol.*, 48:213-235

Steefel, C. I. and A. C. Lasaga, 1994. A coupled model for transport of multiple chemical species and kinetic precipitaion/dissolution reactions with application to reactive flow in single phase hydrothermal systems, *Am. J. Sci.*, 294, 529-592

Steefel, C.I. and K.T.B. MacQuarrie, 1996. Approaches to modeling reactive transport in porous media. Ch 2 in *Reactive Transport in Porous Media, Eds.:* Lichtner, P.C., C.I. Steefel, and E.H. Oelkers, Rev. Mineral. 34, Mineralogical Society of America, Washington, DC.

Valocchi, A. J., and M. Malmsted, 1992. Accuracy of operator splitting for advection-dispersion-reaction problems, *Water Resour. Res*., 28(5):1471-1476.

Yeh, G.-T., and V. S. Tripathi, 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components, *Water Resour. Res., 25:* 93-108.