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Daniel Jara, Jean-Raynald de Dreuzy, Benoit Cochebin. TReacLab: An object-oriented implementation of non-intrusive splitting methods to couple independent transport and geochemical software. *Computers & Geosciences*, 2017, 109, pp.281-294. 10.1016/j.cageo.2017.09.005 . insu-01588325

HAL Id: insu-01588325

<https://insu.hal.science/insu-01588325v1>

Submitted on 15 Sep 2017

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Accepted Manuscript

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PII: S0098-3004(17)30251-0

DOI: [10.1016/j.cageo.2017.09.005](https://doi.org/10.1016/j.cageo.2017.09.005)

Reference: CAGEO 4019

To appear in: *Computers and Geosciences*

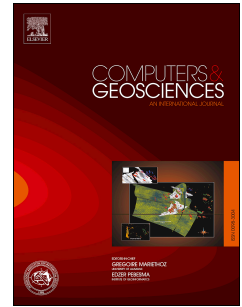
Received Date: 6 March 2017

Revised Date: 1 September 2017

Accepted Date: 7 September 2017

Please cite this article as: Jara, D., Dreuzy, J.-R.d., Cochetin, B., TReacLab: An object-oriented implementation of non-intrusive splitting methods to couple independent transport and geochemical software, *Computers and Geosciences* (2017), doi: 10.1016/j.cageo.2017.09.005.

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1 TReacLab: an object-oriented implementation of non-intrusive
2 splitting methods to couple independent transport and geochemical
3 software

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8 **Abstract**

9 Reactive transport modeling contributes to understand geophysical and geochemical processes
10 in subsurface environments. Operator splitting methods have been proposed as non-intrusive
11 coupling techniques that optimize the use of existing chemistry and transport codes. In this
12 spirit, we propose a coupler relying on external geochemical and transport codes with
13 appropriate operator segmentation that enables possible developments of additional splitting
14 methods. We provide an object-oriented implementation in TReacLab developed in the
15 MATLAB environment in a free open source frame with an accessible repository. TReacLab
16 contains classical coupling methods, template interfaces and calling functions for two
17 classical transport and reactive software (PHREEQC and COMSOL). It is tested on four
18 classical benchmarks with homogeneous and heterogeneous reactions at equilibrium or
19 kinetically-controlled. We show that full decoupling to the implementation level has a cost in
20 terms of accuracy compared to more integrated and optimized codes. Use of non-intrusive
21 implementations like TReacLab are still justified for coupling independent transport and
22 chemical software at a minimal development effort but should be systematically and carefully
23 assessed.

24 **Keywords:** Porous media; Reactive transport; Operator splitting; Object-oriented
25 programming.

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27 **1. Introduction**

28 The fate of chemical species in geological media results from the interaction of physical
29 transport and chemical reactivity (Steeffel *et al.*, 2005). Understanding how they interact
30 requires field and laboratory studies as well as numerical models. Numerical models are
31 important for building predictive scenarios where experiments are limited spatially and
32 temporally, as in long-term nuclear waste disposal assessment (Marty *et al.*, 2014; Thouvenot
33 *et al.*, 2013; Trotignon *et al.*, 2007). On the physical transport side, extensive work in applied
34 mathematics and computational science has provided widely-used software for single and
35 multi-phase flows as well as transport of chemical species such as MODFLOW (McDonald
36 and Harbaugh, 1988), MT3DMS (Zheng and Wang, 1999), HYDRUS (Kool and Van
37 Genuchten, 1991), COMSOL (COMSOL, 2010), FEFLOW (Diersch, 1996), MRST (Lie,
38 2014), and TOUGH2 (Pruess *et al.*, 1999). On the chemistry side, geochemical software have
39 implemented a wide range of chemical functions and reactions, including equilibrium aqueous
40 speciation, equilibrium mineral dissolution/precipitation, gas phase exchange, ion exchange,
41 redox reactions, and kinetic reactions. Some of these software are PHREEQC (Parkhurst and
42 Appelo, 1999), GEMS (Kulik *et al.*, 2013), CHEPROO (Bea *et al.*, 2009), MINTEQA
43 (Peterson *et al.*, 1987), CHESS (Van der Lee, 2002), and Geochemist's Workbench (Bethke,
44 2007).

45 To combine physical and chemical reactivity, couplers have been developed between
46 transport and geochemical codes such as PHAST for coupling HST3D and PHREEQC
47 (Parkhurst *et al.*, 2004), HP1 for HYDRUS and PHREEQC (Šimůnek *et al.*, 2006), PHT3D

48 for MT3DMS and PHREEQC (Prommer *et al.*, 1999), HYTEC for RT1D/R2D2/METIS and
49 CHESS (van der Lee *et al.*, 2003), OpenGeoSys-GEMS (Kulik *et al.*, 2013) and iCP for
50 COMSOL and PHREEQC (Nardi *et al.*, 2014), UTCHEM-IPhreeqc and
51 UTCHEM-EQBATCH (Kazemi Nia Korrani *et al.*, 2015, 2016), multicomponent transport
52 software-IPhreeqc (Muniruzzaman and Rolle, 2016), FEFLOW-IPhreeqc (MIKE(DHI),
53 2016), Lattice Boltzmann transport software-IPhreeqc (Patel *et al.*, 2013). Most of the
54 previously cited codes have embedded the coupling method with the geochemical and
55 transport methods to enhance global performance and reliability. Here, in order to gain
56 flexibility, we propose in our code TReacLab a complementary development in the form of an
57 ensemble of Operator Splitting methods (OS) with a generic set of interfaces to transport and
58 reaction operators. In this context, OS decouples chemistry from transport as opposed to
59 global implicit solvers, which have been proven to be more accurate but less flexible
60 (Hammond *et al.*, 2012; Hammond *et al.*, 2014; Mayer, 2000; Steefel, 2009; Zhang, 2012).
61 TReacLab is designed as an open toolbox where additional OS techniques can be
62 implemented and benchmarked. Other transport and geochemical codes may also be used at
63 the minimal cost of developing the necessary interfaces. TReacLab is written in MATLAB
64 based on a series of abstract classes using object-oriented programming (Commend and
65 Zimmermann, 2001; Register, 2007; Rouson *et al.*, 2011).

66 After recalling in section 2 the reactive transport and OS formalism used, we present in
67 section 3 our OS implementation. We especially show how to implement alternative OS
68 methods and how to connect other transport and geochemical codes. Methods are assessed
69 and discussed on the basis of 3 benchmarks in section 4.

70 **2. Numerical model**71 **2.1. Reactive transport equation**72 The reactive transport equation can be written in a general way as (Saaltink *et al.*, 1998):

$$\frac{\partial \theta c}{\partial t} = ML(c) + \theta S_e^t r_e + \theta S_k^t r_k + Q, \quad (1)$$

73 where c is the vector of concentrations for N_s chemical species in the system. θ is a diagonal
 74 matrix containing the porosity or volumetric content of the phase. M is a diagonal matrix that
 75 specifies whether a species is mobile or immobile. Its diagonal elements are 1 or 0
 76 accordingly. S_k^t and S_e^t are the transposed stoichiometric matrix for kinetic and equilibrium
 77 reactions, respectively. r_e and r_k ($\text{ML}^{-3}\text{T}^{-1}$) are the reaction rates of the N_e equilibrium and N_k
 78 kinetic reactions, respectively. Q is the external sink/source term ($\text{ML}^{-3}\text{T}^{-1}$). L is the transport
 79 operator ($\text{ML}^{-3}\text{T}^{-1}$), which includes advection and diffusion. In the following, we consider
 80 only single-phase flow:

$$L(c) = \nabla \cdot [\mathbf{D}\nabla c - \theta \mathbf{v}c]. \quad (2)$$

81 \mathbf{D} (L^2T^{-1}) is the effective dispersion-diffusion tensor (Bear, 1972). The velocity \mathbf{v} (LT^{-1}) is
 82 computed in a pre-processing phase, which can be decoupled from the reactive transport
 83 problem as long as hydraulic properties are not modified by the chemical reactivity. The
 84 chemical system can be generically written as the combination of the N_e equilibrium reactions:

$$\Phi_e(c) = 0, \quad (3)$$

85 and of the N_k kinetically-controlled reactions:

$$r_k = \phi_k(c). \quad (4)$$

86 The reactive transport problem is thus made up of the N_s mass balance equation (1) and of the
 87 $N_e + N_k$ equilibrium and kinetic equations (3) and (4). Its unknowns are the concentrations c
 88 and the reaction rates r_e and r_k . The chemical equilibrium system (3) is composed of the
 89 conservation equation and of the mass action law, relating reactants and products (Apoung-
 90 Kamga *et al.*, 2009; Molins *et al.*, 2004):

$$S_e \log(c) = \log(K), \quad (5)$$

91 where K is the vector of equilibrium constants.

92 Components u are generally introduced when considering equilibrium reactions (Saaltink *et*
 93 *al.*, 2011):

$$u = Uc, \quad (6)$$

94 where U is the component matrix (Fang *et al.*, 2003; Friedly and Rubin, 1992; Hoffmann *et*
 95 *al.*, 2012; Krättele and Knabner, 2005; Steefel *et al.*, 2005). They are $N_s - N_e$ linear
 96 combinations of chemical species that are not modified by equilibrium reactions (Molins *et*
 97 *al.*, 2004; Morel and Hering, 1993):

$$US_e^T r_e = 0. \quad (7)$$

98 The component matrix is not unique. However, its application to equation (1) always leads to
 99 a reduced system without the equilibrium rates but with the components u (Molins *et al.*,
 100 2004; Saaltink *et al.*, 1998):

$$\frac{\partial u}{\partial t} = UML(c) + U\theta S_k^e r_k + UQ. \quad (8)$$

101 The reactive transport problem is then made up of the $2N_s - N_e + N_k$ equations (3-6) and (8)
 102 for the same number of unknowns u , c and r_k .

103 Under the assumption that solid species are not transported and all species have the same
 104 diffusion coefficient (i.e. $UML(c) = UL(u)$). Equation (8) classically gives the two following
 105 formulations TC and CC (Amir and Kern, 2010):

$$\text{TC:} \quad \frac{\partial u}{\partial t} = L(u_a) + U\theta S_k^e r_k + UQ. \quad (9)$$

$$\text{CC:} \quad \frac{\partial u_a}{\partial t} + \frac{\partial u_f}{\partial t} = L(u_a) + U\theta S_k^e r_k + UQ. \quad (10)$$

106 where $u_a = UMc$ and $u_f = U(I - M)c$ are the aqueous and fixed components. In the TC
 107 formulation, the fixed species concentration are deducted from the solution in the total
 108 component concentration (T) and the solute concentration (C). In the CC formulation, the
 109 total component concentration is divided in aqueous and fixed components.

110 2.2. Usual first-order sequential non-iterative and iterative approaches

111 In this section, we show how the reactive transport problem can be solved using independent
 112 transport and chemical solvers. We distinguish the sequential non-iterative and iterative
 113 approaches respectively based on TC and CC formulations. For the sequential non-iterative
 114 approach, we extract from the TC formulation, the transport operator in which we keep the
 115 sink/source term:-

$$\frac{\partial u}{\partial t} = L(u_a) + UQ. \quad (11)$$

116 The chemical operator derives from equations (3-6), and (8). Note that it does not contain any
 117 source/sink term, as it has been included in the transport equation:

$$\begin{aligned} \frac{\partial u}{\partial t} &= US_k^c r_k \\ r_k &= \phi_k(c) \end{aligned} \quad (12)$$

$$u = Uc$$

$$\phi_a(c) = 0.$$

118 This is still a system of $2N_s - N_e + N_k$ equations for the same number of unknowns. This
 119 decoupled system can be solved with the classical sequential non-iterative approach using an
 120 explicit integration of temporal derivatives (herein, we assume forward Euler). The solution at
 121 time step $n+1$ can be obtained from the solution at time step n , with the following successive
 122 application of the transport and chemical operators in a sequential approach:

$$u^* = u_n + \Delta t(L(u_n) + UQ)$$

$$\begin{cases} u^* = U c_{n+1} \\ \phi_s(c_{n+1}) = 0 \end{cases} \quad (13)$$

$$r_{k_{n+1}} = \phi_k(c_{n+1})$$

$$u_{n+1} = u^* + \Delta t U S_k^{\xi} r_{k_{n+1}}$$

123 The transport operator (11) is applied to the components. Then the chemical operator is
 124 applied with the updated mobile components for speciation between fixed and solute
 125 concentrations. In the specific case where chemical reactions are all at equilibrium and no
 126 kinetics is involved, a TC formulation is used to fully decouple (de Dieuleveult *et al.*, 2009).
 127 In such case the decoupling does not then rely on operator splitting, but on a block
 128 Gauss-Seidel method. When the stability conditions of the explicit integration are too much
 129 constraining, implicit schemes should be used instead within a sequential iterative approach
 130 (Carrayrou *et al.*, 2004; de Dieuleveult and Erhel, 2010; Yeh and Tripathi, 1989):

$$u_{n+1} = u_n + \Delta t[L(u_{n+1}) + \theta S_k^{\xi} r_{k_{n+1}} + UQ]$$

$$\begin{cases} u_{n+1} = U c_{n+1} \\ \phi_s(c_{n+1}) = 0 \end{cases} \quad (14)$$

$$r_{k_{n+1}} = \phi_k(c_{n+1}).$$

131 Classical Picard's method have been extensively used to solve such kind of problems:

$$u_{n+1}^{k+1} = u_n + \Delta t [L(u_{n+1}^{k+1}) + \theta S_k^t r_{k_{n+1}}^k + UQ]$$

$$\begin{cases} u_{n+1}^{k+1} = U c_{n+1}^{k+1} \\ \Phi_s(c_{n+1}^{k+1}) = 0 \end{cases} \quad (15)$$

$$r_{k_{n+1}}^{k+1} = \Phi_k(c_{n+1}^{k+1}),$$

132 where k is the index of the Picard iteration method instantiated by:

$$u_{n+1}^{k=1} = u_n \quad (16)$$

$$r_{k_{n+1}}^{k=1} = r_{k_n}.$$

133 We recall the necessity to check the consistency of the temporal integration scheme with the
 134 Operator Splitting method chosen. With this decomposition, explicit first-order scheme
 135 naturally leads to sequential non-iterative approach. The implicit first-order scheme requires a
 136 sequential iterative approach. Other choices are possible and might reduce errors depending
 137 on the chemical system (Barry *et al.*, 1996). As it should be possible to test and benchmark
 138 them at a reduced development cost, we use a generic decoupling formalism that can be used
 139 to implement a broad range of schemes.

140 2.3. Generic operator splitting implementation

141 The reactive transport system can be generically split in two operators. Using the formalism
 142 of Gasda *et al.* (2011), equation (1) can be written as:

$$\frac{\partial Z}{\partial t} = \mathcal{L}_1 Z + \mathcal{L}_2 Z, \quad Z(t=0) = Z_0, \quad 0 \leq t \leq T, \quad (17)$$

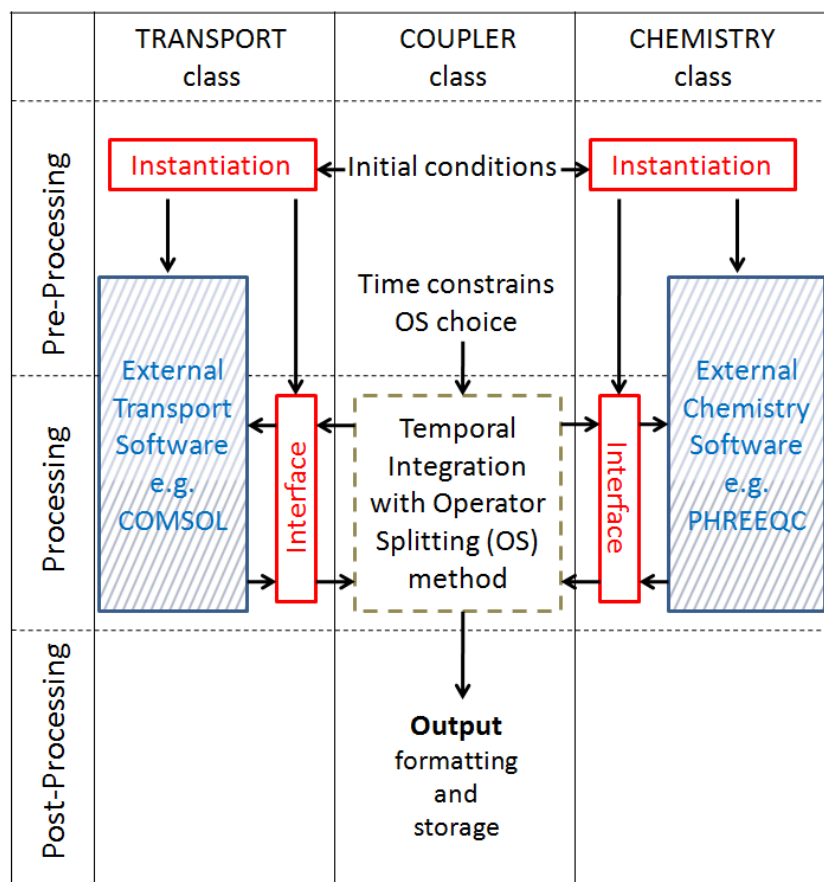
143 where Z is the unknown, \mathcal{L}_1 and \mathcal{L}_2 can be equation (11) and (12), respectively. Other
 144 decomposition are possible, e.g. the transport operator can be subdivided into an advection
 145 and a diffusion-dispersion operator (Clement *et al.*, 1998), or one operator might contain
 146 advection-reaction and the other diffusion (Liu and Ewing, 2005). Each operator will be
 147 solved separately for a splitting time step $\Delta t = t^{n+1} - t^n$ using adapted numerical methods.

148 The generic operator splitting methods implemented into the Toolbox are the sequential
 149 splitting, additive splitting, Strang splitting, symmetrically weighted splitting, and alternating
 150 method (Appendix A). Assuming exact integration of the operators and homogeneous
 151 boundary conditions in equation (18), the first two have a first-order temporal truncation
 152 error, and the following three a second-order one (Hundsdorfer and Verwer, 2013). Since the
 153 operators are usually solved using numerical methods, the global order of such approaches
 154 might be modified because of the order of the numerical methods used for each operator
 155 (Barry *et al.*, 1996; Csomós and Faragó, 2008). The alternating splitting increases the order of
 156 the sequential splitting if the time steps are small enough (Simpson and Landman, 2008;
 157 Valocchi and Malmstead, 1992).

158 3. Operator splitting implementation and software organization

159 We provide in TReacLab an object-oriented toolbox for the non-intrusive operator splitting
 160 methods of the previous section. TReacLab is organized along three main components for
 161 coupling transport and reactivity, and proceeds in three pre-processing, processing and
 162 post-processing phases (Figure 1). These three components correspond to the three

163 well-identified coupler, transport and chemistry classes. The three classes are fully segmented
164 and exchange information through interfaces. Segmentation ensures that any of the three
165 coupler, transport and chemistry classes can be replaced without modifications of any of the
166 two other ones. The solution of the reactive transport problem after spatial discretization
167 eventually consists in the temporal integration with the chosen OS technique, which
168 iteratively calls transport and geochemical solvers through interfaces (Figure 1, middle row).
169 This is the core of the simulation that we identify as the processing phase. It is generic and
170 does not require at run time any further specification of transport, reactivity and coupler
171 methods. Standard error management techniques are used to stop the algorithm when any of
172 the integration method of the three classes fails, stopping the running process and returning
173 adapted error messages.



174

175 *Figure 1: General software organization of TReacLab with the three coupler, transport and*
 176 *chemistry classes in columns, and the three pre-processing, processing, and post-processing*
 177 *phases in rows. Generic components represented in black are the organization and the*
 178 *coupler class. External software for transport and chemistry are represented in blue with*
 179 *hatched line (cannot be modified). Red boxes highlight the instantiation and interface*
 180 *methods that must be developed when connecting new transport or chemistry software.*

181 The processing phase can be generic because all specifications of the coupler, transport, and
 182 chemistry classes are performed in a pre-processing phase (Figure 1, first row). The
 183 pre-processing phase consists in the instantiation of the coupler, transport and chemical
 184 classes, in the preparation of the interfaces that will transfer information and in the
 185 specifications of the initial conditions. As detailed in Appendix B, instantiations are code
 186 dependent. Instantiation can be done externally for example with the definition of a transport

187 or chemical problem through the graphical user interface of software like COMSOL or
188 PHREEQC. It can also be done internally by a method within TReacLab specifying the inputs
189 and parameters to existing interfaces like IPhreeqc (Charlton and Parkhurst, 2011),
190 PhreeqcRM (Parkhurst and Wissmeier, 2015), or COMSOL livelink (COMSOL, 2010). Even
191 when instantiation is complex, it remains independent for each of the three classes.
192 Cross-dependencies and feedback between transport and reactivity like density-driven flows
193 with reacting species are not supported at this stage, although they may be important in some
194 applications like CO₂ sequestration (Abarca *et al.*, 2013).

195 Pre-processing phase specifies the initial conditions and transfers them to the coupler in
196 charge of starting the numerical integration. Post-processing is generic and only consists in
197 formatting and storing output concentrations and solver performances (Figure 1, bottom row).
198 Specifications are all restricted to the instantiation of the software and interface in the
199 pre-processing phase while processing and post-processing remain fully generic. Connections
200 between specific algorithms and generic structures are done by interfaces. Appendix B
201 provides a detailed description of the transport and chemistry classes, defining the interfaces
202 to the external codes.

203 **4. Examples and benchmarks**

204 The three following examples validate the methods and illustrate the implementation
205 presented in sections 2 and 3. The three of them are based on a 1D hydraulically
206 homogeneous system with steady-state flow and uniform dispersion (equation (2)).The
207 examples are compared visually against analytical solution or well-know numerical software.
208 Moreover, we show a convergence study for the first case being the reference solution the
209 numerical solution with finest time resolution.

210 The four examples display evolving degrees of complexity both in terms of chemical systems
211 and in terms of software called for transport and reactivity, software versions are given in
212 Table 1. The first example is a single-species transport with first-order decay. The transport
213 solver is COMSOL and the chemical solver is a simple analytical solution. This example is
214 used to assess the different coupling algorithms implemented and to check the implementation
215 of the interface with COMSOL. The second example is an equilibrium
216 precipitation/dissolution chemical system in a 1D hydraulically homogeneous system.
217 Chemical solver is IPhreeqc. Several solvers have been compared for the transport solver,
218 both to check IPhreeqc interface implementation and to evaluate the effect of the transport
219 solver. The third example is the most advanced in terms of chemistry. Chemical reactions are
220 partly in equilibrium and partly kinetically controlled. They involve precipitation and
221 dissolution reactions. The chemical code is PhreeqcRM. It is used in combination with
222 COMSOL as transport solver. The last problem face a 2D unsaturated system where transport
223 is modeled by Richards equation and solved by COMSOL. Chemistry is solved by
224 PhreeqcRM. These four test cases have been chosen to check the implementation and assess
225 the coupling methods developed. They are also simple enough from the development point of
226 view to be taken as starting points to model more advanced chemical systems and transport
227 conditions.

Software	Version
MATLAB	R2013b
COMSOL	4.3b
PHREEQC	3.3.7
IPhreeqc	3.3.7
PhreeqcRM	3.3.9

228 *Table 1: Software versions.*

229 **4.1. Single-species transport with first-order decay**

230 A single-species transport with first-order decay using different OS methods is compared to
 231 an analytical solution (Van Genuchten and Alves, 1982). The reactive transport system
 232 contains a single solute species of concentration c :

$$\frac{\partial c}{\partial t} = L(c) - kc, \quad (18)$$

233 where L is given by equation (2). Equation (18) can straightforwardly be separated into
 234 transport and chemistry operators corresponding to the two right-hand side terms.

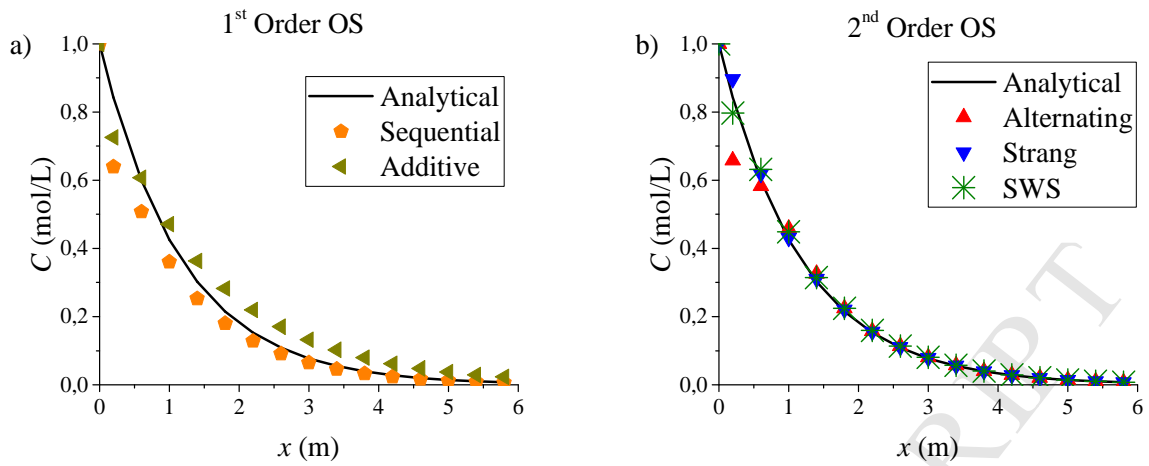
235 At time 0, the solute concentration is 0 in the domain ($c(x, t=0) = 0$). The concentration at the
 236 left boundary is constant and equal to 1 mol/m³ ($c(x = 0, t) = 1$ mol/m³). The boundary
 237 condition on the right side of the domain is a perfectly absorbing condition ($c(x = x_{\max}, t) = 0$).

238 Parameters are derived from Steefel and MacQuarrie (1996) and given in Table 2. The solver
 239 for transport is COMSOL and an analytical solution is used for the first-order decay. Solute
 240 concentration progressively invades the domain from the left boundary with a smooth profile
 241 resulting from the combination of dispersion and decay (Figure 2). Second-order methods
 242 perform much better than first-order methods as expected. Errors are more pronounced at the
 243 inlet boundary condition on the left side of the domain where the concentration is higher

244 (Steeffel and MacQuarrie, 1996; Valocchi and Malmstead, 1992). The sequential splitting
 245 method with the transport operator performed first overestimates the amount of reaction for
 246 the whole domain since it considers that all incoming solute is getting in without decay for the
 247 full first time step. If the sequence of operators is exchanged, namely first chemistry is solved,
 248 and then transport is solved, the amount of reaction is underestimated. The second-order
 249 alternating splitting, which alternates between transport-chemistry and chemistry-transport
 250 steps, shows strong improvement with compensations between overestimation in the first
 251 application of the chemical operator and underestimation in the second application of the
 252 chemical operator (Simpson and Landman, 2008; Valocchi and Malmstead, 1992).

Parameter	Value
v [m/y]	100
D [m ² /y]	20
k [y ⁻¹]	100
x_{\max} [m]	6
Δx [m]	0.4
Δt [y]	$4 \cdot 10^{-3}$

253 *Table 2: Parameters for the single-species transport with first-order decay benchmark. v is*
 254 *the velocity, D is the dispersion coefficient, k is the decay rate, x_{\max} is the length of the 1D*
 255 *column, Δx is the grid size, and Δt is the time step.*



256 *Figure 2: Comparison of first- and second-order OS for the single-species transport with*
 257 *first-order decay at $t = 0.5$ y. Parameters are given in Table 2. Analytical solution is derived*
 258 *from Van Genuchten and Alves (1982).*

259 The error at time $t = 0.5$ y is taken as the quadratic relative difference over the domain of the
 260 finest time step of the numerical solution and the numerical solutions for the corresponding
 261 time step, c_{NF} and c_N respectively:

$$\|e\|_2 = \sqrt{\sum_{i=1}^{N_x} \left(\frac{c_{NF}^i(t) - c_N^i(t)}{c_{NF}^i(t)} \right)^2}. \quad (19)$$

262 Table 3 displays the values for evolving time steps and shows that all methods converge with
 263 the time. The reference finest time step for each method has been $\Delta t = 2 \cdot 10^{-4}$ s (i.e. $c_{NF}^i(t)$
 264 value). While all methods perform well, the sequential method is more accurate than the
 265 additive one and second-order methods are overall more accurate than first-order methods.
 266 The performance on convergence arranged on descending order is given by Strang,
 267 symmetrically weighted splitting, alternating, sequential and additive.

		1 st order		2 nd order		
		Additive	Sequential	Alternating OS	Strang	SWS
$\Delta x = 0,4 \text{ m}$	$\Delta t \text{ (y)}$					
	$4 \cdot 10^{-3}$	1,107	0,1667	0,075	0,032	0,049
	$2 \cdot 10^{-3}$	0,514	0,079	0,032	0,026	0,028
	$4 \cdot 10^{-4}$	0,114	0,019	0,029	0,031	0,029

268 Table 3: Error $\|e\|_2$ of equation (19) for the single-species transport with first-order decay
 269 with different OS methods and splitting time steps.

270 4.2. Calcite dissolution

271 Calcite dissolution and dolomite formation has become a classical benchmark for reactive
 272 transport problems with sharp precipitation/dissolution fronts (Beyer *et al.*, 2012; Engesgaard
 273 and Kipp, 1992; Prommer *et al.*, 1999). Progressive introduction of magnesium calcium in a
 274 domain at equilibrium between calcium carbonate in solution and calcite (CaCO_3) dissolves
 275 the calcite and precipitates dolomite ($\text{CaMg}(\text{CO}_3)_2$). This chemical system has been modeled
 276 with the physical and chemical parameters given by Table 4, Table 5, and Table 6. Chemical
 277 concentrations are initially homogeneous. At the initial time ($t = 0$), the chemical system is
 278 destabilized with the introduction of magnesium instead of calcium at the upper boundary
 279 condition ($x = 0$), inducing the dissolution/precipitation process. The boundary condition at
 280 the downstream limit (x_{max}) is a simple outflow of the solutes.

281 Here, we show how transport solvers can be applied and validate our interface to IPhreeqc.
 282 IPhreeqc performs the computation of components, aqueous speciation, precipitation and
 283 dissolution reactions (Charlton and Parkhurst, 2011). The database used is
 284 'NAPSI_290502(260802).dat'. Transport is solved either with COMSOL Multiphysics
 285 (COMSOL, 2012), with a finite difference spatial discretization and forward Euler time

286 integration, derived from built-in pdepe function of MATLAB (Skeel and Berzins, 1990).
 287 Transport and chemistry are coupled through the simple sequential approach of equations
 288 (A.1)-(A.3). PHREEQC is independently run as 1D reactive transport solver for general
 289 comparison.

Parameter	Value
v [m/s]	10^{-5}
D [m ² /s]	$6.7 \cdot 10^{-8}$
x_{\max} [m]	0.25
Δx [m]	0.01
Δt [s]	50

290 *Table 4: Physical parameters for the calcite dissolution benchmark. v is the average velocity,*
 291 *D is the dispersion coefficient, x_{\max} is the maximum length of the column, Δx is the grid size,*
 292 *and Δt is the time step.*

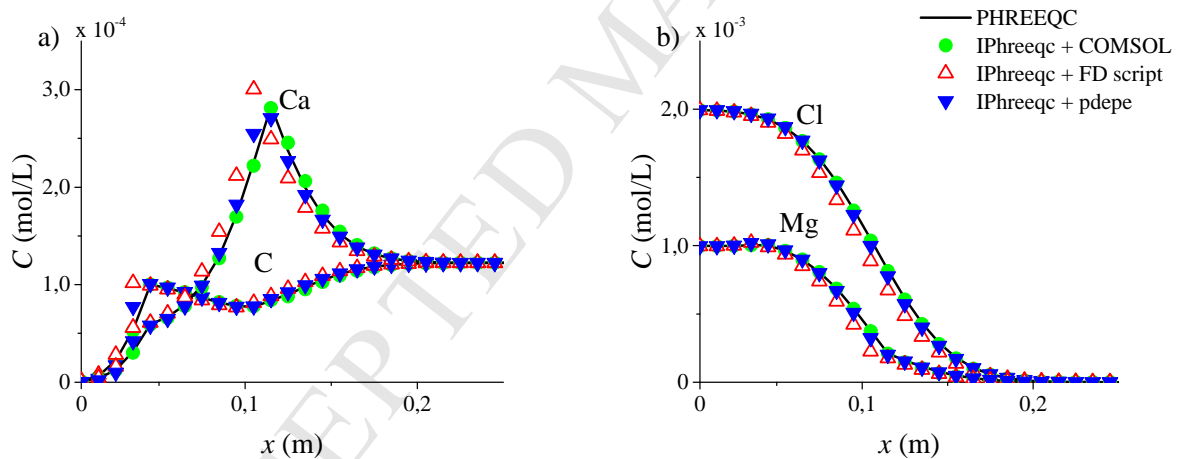
Chemical Component and Species	Initial value	Boundary value at $x=0$
Ca [mol/L]	$1.23 \cdot 10^{-4}$	0
C [mol/L]	$1.23 \cdot 10^{-4}$	0
Cl [mol/L]	0	$2 \cdot 10^{-3}$
Mg [mol/L]	0	10^{-3}
pH [-]	9.91	7
Calcite [mol/L]	$2 \cdot 10^{-4}$	-
Dolomite [mol/L]	0	-

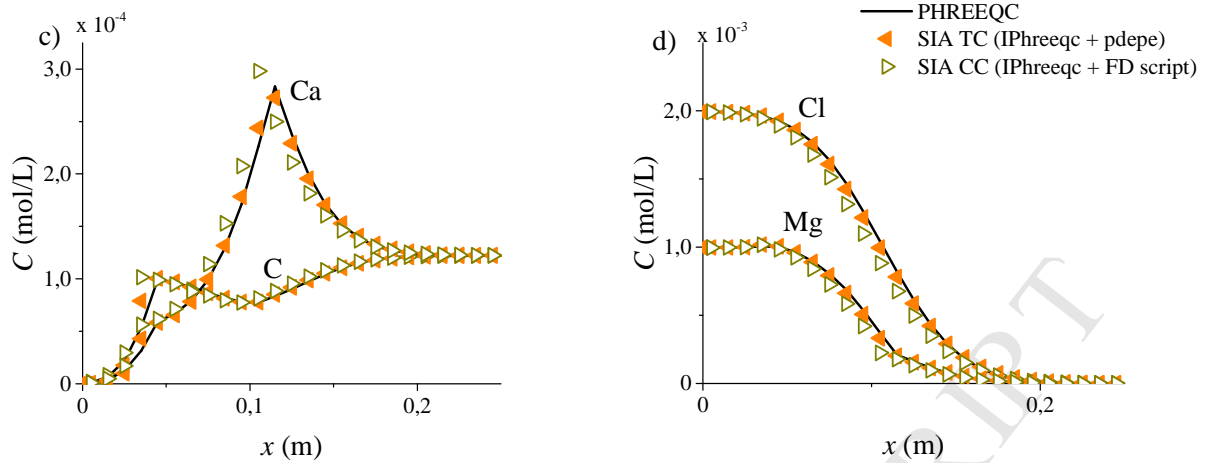
293 *Table 5: Calcite dissolution benchmark initial and boundary values for aqueous components*
 294 *and mineral species. In PHREEQC, components are called elements.*

Homogeneous reactions	log (K)
$2H^+ + 2e^- \leftrightarrow H_2$	-3.1055
$2H_2O - 4H^+ - 4e^- \leftrightarrow O_2$	-85.9862
$HCO_3^- + 9H^+ + 8e^- - 3H_2O \leftrightarrow CH_4$	27.8493
$H_2O - H^+ \leftrightarrow OH^-$	-13.9995
$H^+ - H_2O + HCO_3^- \leftrightarrow CO_2$	6.3519
$HCO_3^- - H^+ \leftrightarrow CO_3^{2-}$	-10.3289
$Ca^{2+} - H^+ + HCO_3^- \leftrightarrow CaCO_3$	-7.1048
$Ca^{2+} + HCO_3^- \leftrightarrow CaHCO_3^+$	1.1057
$Ca^{2+} + H_2O - H^+ \leftrightarrow CaOH^+$	-12.78
$Mg^{2+} - H^+ + HCO_3^- \leftrightarrow MgCO_3$	-7.3492
$Mg^{2+} + HCO_3^- \leftrightarrow MgHCO_3^+$	1.0682
$Mg^{2+} + H_2O - H^+ \leftrightarrow MgOH^+$	-11.44
Homogeneous reactions	
Calcite	
$CaCO_3 \leftrightarrow Ca^{2+} - H^+ + HCO_3^-$	1.849
Dolomite	
$CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} - 2H^+ + 2HCO_3^-$	4.118

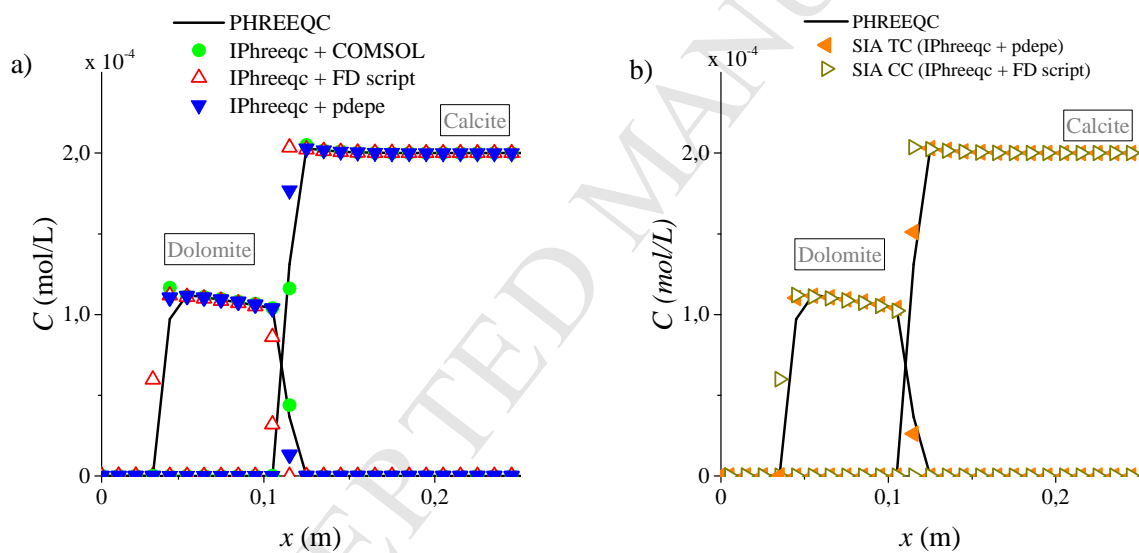
296 *Table 6: Chemical system of the calcite dissolution benchmark. The upper part comprises the*
 297 *homogeneous equations and the lower part the heterogeneous reactions. The first column*
 298 *shows the equilibrium reactions and the second one the logarithms of equilibrium constants.*

299 Figure 3 and Figure 4 display aqueous and mineral equivalent concentrations at time $t = 10^4$ s.
 300 As magnesium and chloride get in the domain (Figure 3b and Figure 3d), calcite progressively
 301 dissolves and is replaced by dolomite as expected (Figure 4). Some of the calcium remains in
 302 solution and is flushed out (Figure 3a and Figure 3c). Because of the subsequent absence of
 303 calcium in solution, dolomite dissolves again with some increase of calcium in solution
 304 (Figure 3a and Figure 3c). The three different transport solvers give the same tendency as the
 305 PHREEQC solution.





306 *Figure 3: Aqueous concentration profiles at time $t = 10^4$ s.*



307 *Figure 4: Dolomite and calcite equivalent concentration profiles with open and filled symbols*
 308 *respectively at time $t = 10^4$ s.*

309 Although COMSOL leads to good results, it is more than one order of magnitude slower than
 310 the two other transport methods (Table 7). We checked that this large difference in
 311 performances does not come from the numerical method but from the large time required for
 312 COMSOL to start and stop when called numerous times externally. While this might not be

313 an issue for large transport problems for which limitations will rather come from transport
 314 operator, it is a constrain for smaller tests and benchmarks.

Software Coupling	Time
IPhreeqc + COMSOL	668 s
IPhreeqc + FD script	24 s
IPhreeqc + pdepe	40 s

315 *Table 7: Time performance for the calcite dissolution benchmark using a sequential operator*
 316 *splitting.*

317 Whatever the coupling method, the consistency with PHREEQC is overall good. Although
 318 COMSOL uses, as default, implicit time integration schemes for solving the transport
 319 equation instead of the required explicit method, it still compares well with PHREEQC and
 320 the other software couplings. Indeed, the sequential non iterative method requires an explicit
 321 time integration for transport (equation (13)). It is not the case for COMSOL which uses (as
 322 default) a backward differentiation formula temporal integration scheme, which order varies
 323 with the internal time step adaptation (COMSOL, 2012). It thus introduces an additional error
 324 in the coupling scheme (de Dieuleveult *et al.*, 2009). However, by using such stable and
 325 accurate temporal integrations, it enhances the robustness of the transport scheme.

326 **4.3. Mixed equilibrium-kinetic system**

327 We simulate the progressive increase of dissolved species in an atmospheric water infiltrating
 328 a granitic bedrock. This test case is derived from Nardi *et al.* (2014). The hydraulic properties
 329 of the system are found in Table 8. The infiltrating water has much lower concentrations of
 330 dissolved species than the resident water. It interacts with five minerals (Table 9). It is in
 331 equilibrium with calcite. The four other minerals k-feldspar, illite, albite and pyrite are subject
 332 to kinetically controlled dissolution with rates ranging from 10^{-13} to 10^{-11} mol/s. All

333 parameters and rate laws of the simulation are provided in the PHREEQC file of iCP (Nardi *et*
 334 *al.*, 2014). The infiltrating water dissolves calcite to maintain equilibrium, increasing both the
 335 concentration of calcium and the pH of the solution. Other minerals also dissolve and increase
 336 the concentrations of Al and K in solution, however at a much slower rate because of the
 337 kinetic control of the reactions. pH is eventually buffered by the dissolution of illite and
 338 pyrite.

Parameter	Value
v [m/s]	$2.78 \cdot 10^{-6}$ m/s
D [m/s]	$5.55 \cdot 10^{-9}$ m ² /s
x_{\max} [m]	0.08 m
Δx [m]	10^{-3} m
Δt [s]	720 s

339 *Table 8: Parameters for mixed equilibrium-kinetic benchmark. v is the average velocity, D is*
 340 *the dispersion coefficient, x_{\max} is the maximum length of the column, Δx is the grid size, and*
 341 Δt *is the splitting time.*

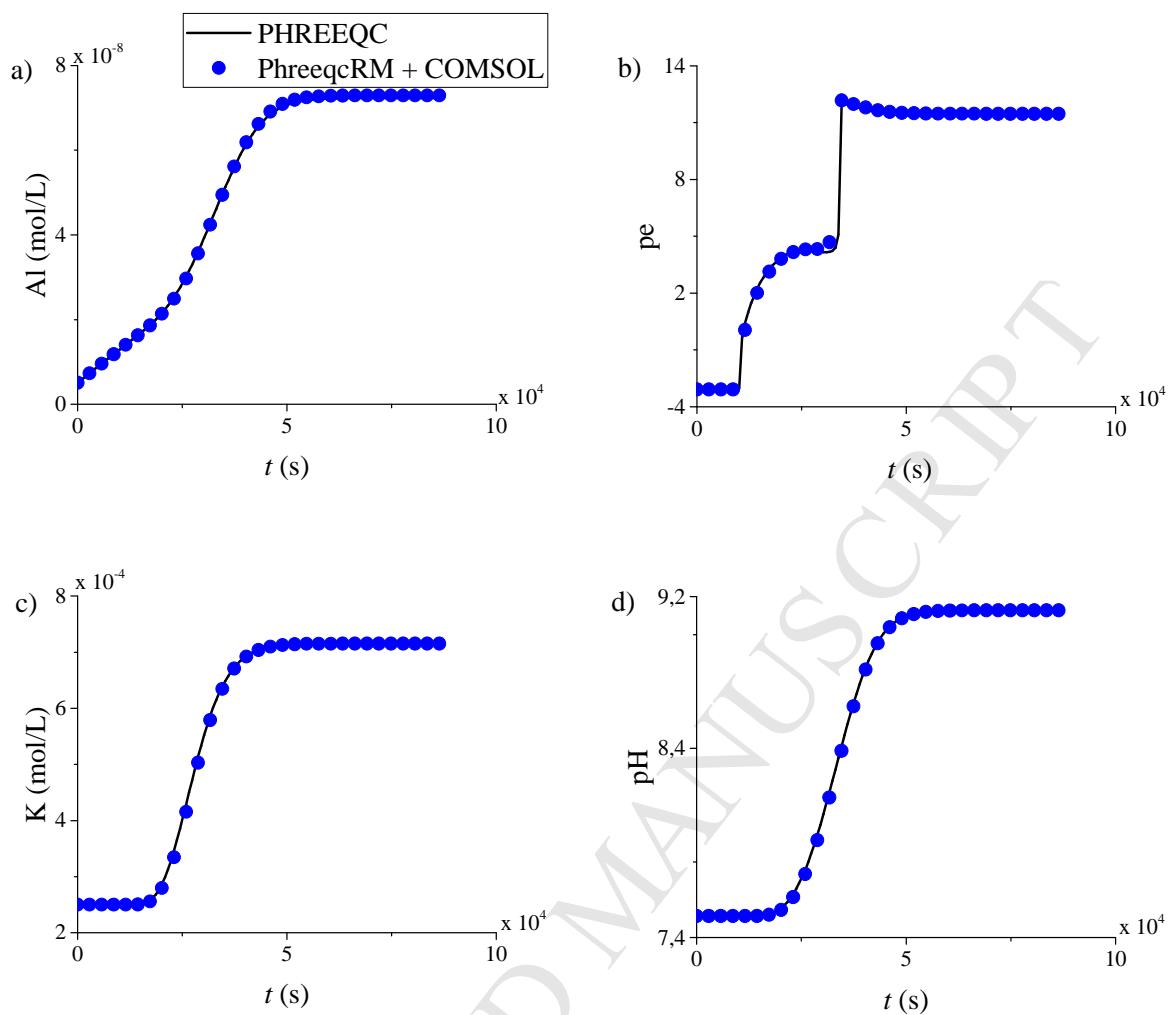
Chemical Component and Species	Initial value	Boundary value
Ca [mol/L]	$1.4 \cdot 10^{-3}$	$3 \cdot 10^{-4}$
C [mol/L]	$4.9 \cdot 10^{-3}$	$1.9 \cdot 10^{-4}$
Cl [mol/L]	$1.1 \cdot 10^{-2}$	$9 \cdot 10^{-4}$
Mg [mol/L]	$7.4 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
Mn [mol/L]	$3.4 \cdot 10^{-6}$	0
S [mol/L]	$9.6 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$
Na [mol/L]	$1.3 \cdot 10^{-2}$	$3 \cdot 10^{-4}$
K [mol/L]	$2.5 \cdot 10^{-4}$	$7.1 \cdot 10^{-4}$
Fe [mol/L]	$7.2 \cdot 10^{-6}$	$5.4 \cdot 10^{-5}$
Sr [mol/L]	0	$6.8 \cdot 10^{-7}$
Si [mol/L]	$2 \cdot 10^{-4}$	$2.5 \cdot 10^{-6}$
Al [mol/L]	$5.1 \cdot 10^{-9}$	10^{-8}
P [mol/L]	$3.8 \cdot 10^{-6}$	0
Br [mol/L]	$1.7 \cdot 10^{-5}$	0
F [mol/L]	$3.1 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$
pH [-]	7.5144	7.3
pe [-]	-3.0836	13.6
Calcite [mol/L]	6.065	-
K-feldspar [mol/L]	0.239	-
Illite [mol/L]	0.144	-
Albite [mol/L]	0.289	-
Pyrite [mol/L]	1.17	-

343 *Table 9: Aqueous components and mineral species for mixed equilibrium-kinetic benchmark.*

344 To simulate this set of reactions, we have chosen PhreeqcRM to assess the flexibility of
 345 TReaCLab. Transport is simulated with COMSOL to benefit from the accurate transport
 346 solver, it uses a variable order (between 1 and 5) backward differentiation formula. In the

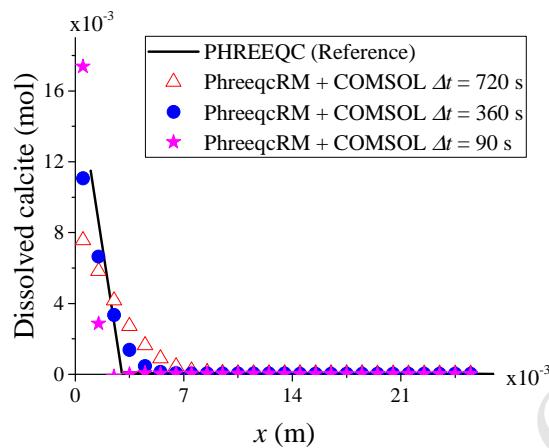
347 presence of both kinetically controlled and equilibrium reactions, both the quality of the
348 transport and reactive integrations and coupling issues may be critical. We choose a simple
349 sequential OS method with the successive integration of transport and reactivity. The results
350 obtained by the coupling of COMSOL and PhreeqcRM are close to the solution given by
351 PHREEQC alone for the dissolved species and kinetically dissolving minerals (Figure 5). The
352 time step of the coupled PhreeqcRM and COMSOL integration has been taken smaller than
353 the characteristic mesh scale transport time and reactive time at least for the kinetical reaction
354 to ensure accurate integrations. The most difficult quantity to get accurately is the calcium
355 concentration because calcite is at equilibrium. The time step must be reduced to recover a
356 steeper reactive front (Figure 6).

357 This more advanced test shows that the computational load should be well balanced between
358 the coupler, transport and chemistry methods. While coupling is the critical component in
359 cases of equilibrium reactions and may even require highly integrated coupling strategies like
360 global implicit methods (Hoffmann *et al.*, 2010; Saaltink *et al.*, 2001), it is not the case for
361 kinetically controlled reactions. In this case of mixed equilibrium kinetic reaction, elementary
362 coupling and accurate transport and reactive solvers can be efficient with small enough time
363 steps where sharp reaction fronts are involved.



364 *Figure 5: Comparison of results between the coupling of PhreeqcRM and COMSOL and*
365 *PHREEQC observed for the mixed equilibrium-kinetic benchmark at the output of the column.*

366

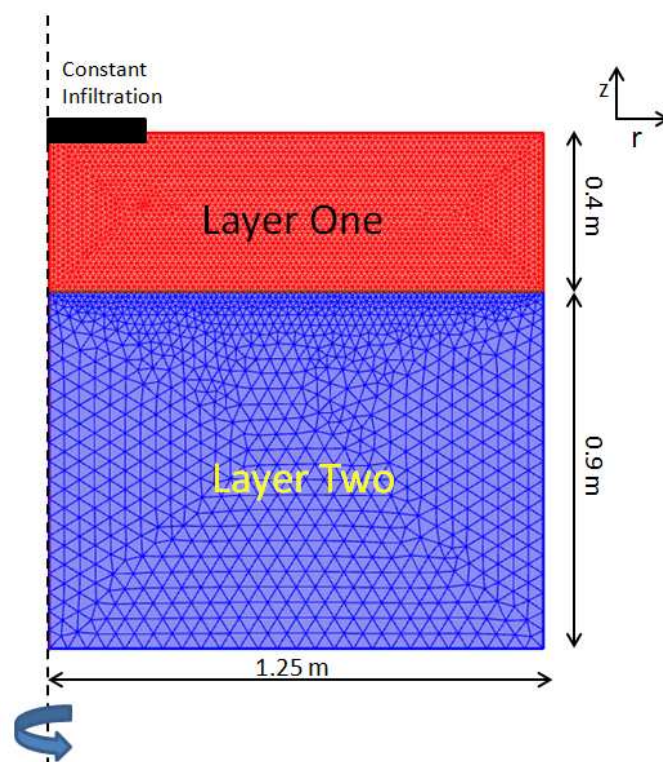


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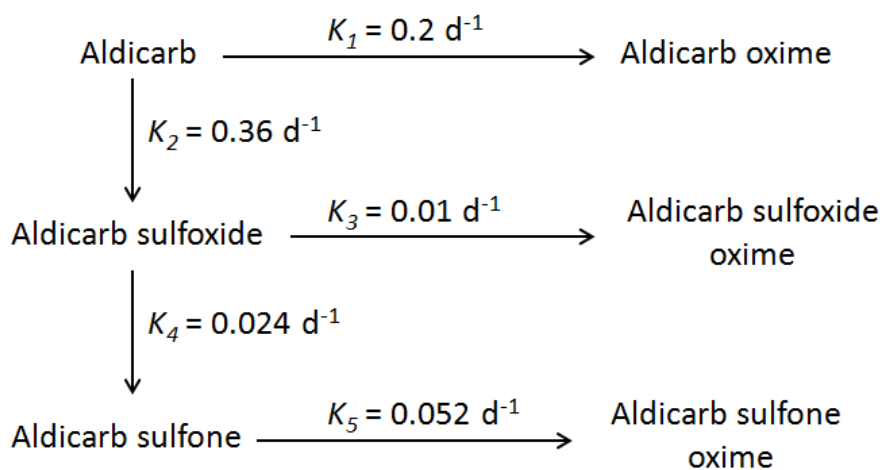
368 *Figure 6: Quantity of dissolved calcite with PhreeqcRM and COMSOL for two different*
 369 *splitting time steps $\Delta t = 720$ s, 360 s and 90 s. PHREEQC independently is used as reference.*

370 4.4. Pesticide infiltration

371 The following benchmark concerns the infiltration in an unsaturated soil column of a
 372 carbamate insecticide (Aldicarb) (MIKE(DHI), 2016; Multiphysics, 2008; Šimůnek *et al.*,
 373 1994; Wissmeier and Barry, 2011). The soil column is a 2D axisymmetric cylinder made up
 374 of two layers with a smaller hydraulic conductivity in the upper layer but higher saturation.
 375 Transport is modeled by Richards' equation and solved by COMSOL (Figure 7). Aldicarb is
 376 transported downwards and sideways from the infiltration (top of the column from $r = 0$ m to
 377 $r = 0.25$ m). Chemistry is described by first-order decay chain reactions (Figure 8), being only
 378 mobile Aldicarb, Aldicarb sulfoxide and Aldicarb sulfone (i.e. the other species are fix
 379 species). These system of ordinary differential equations is solved by PhreeqcRM.



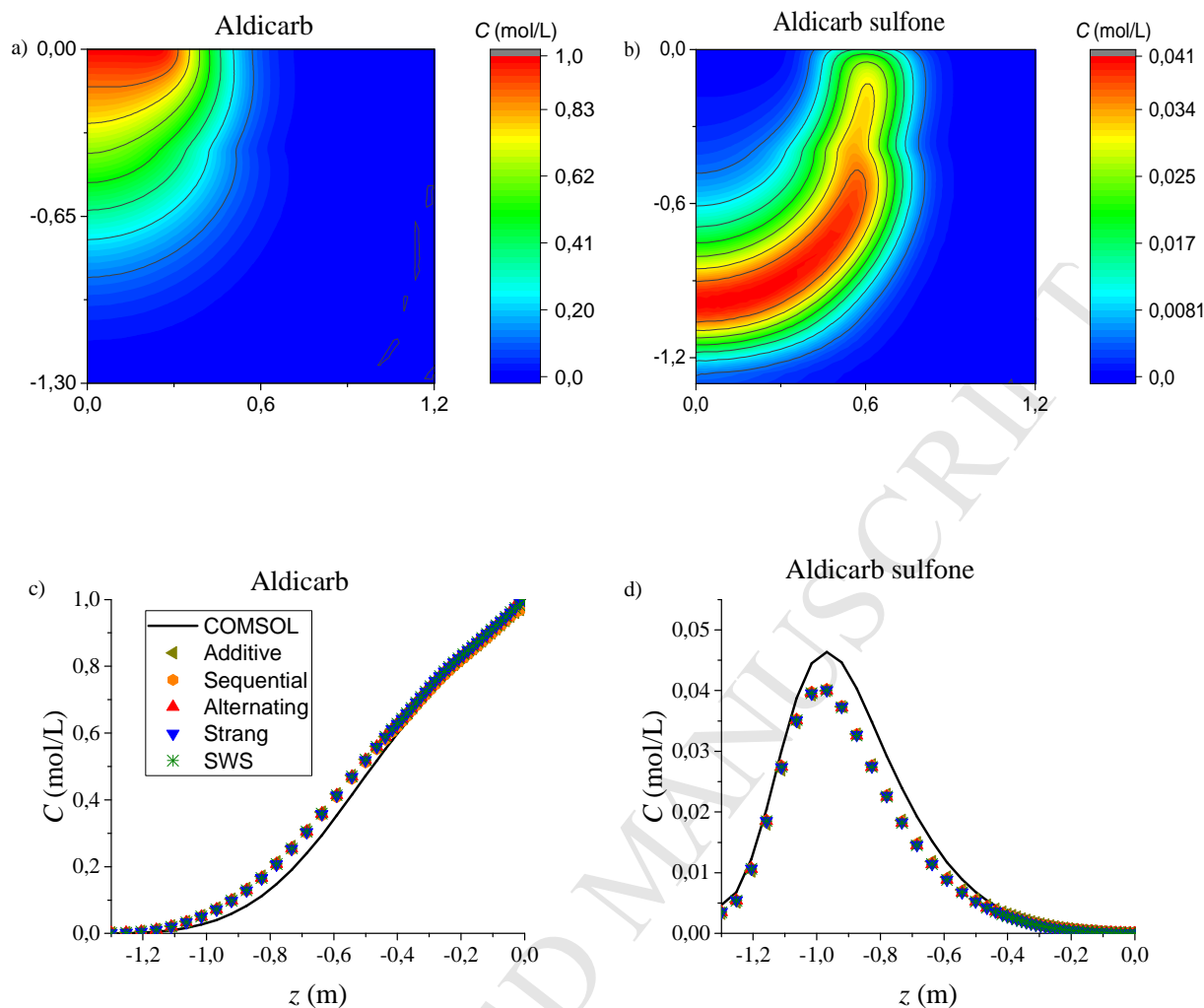
380

381 *Figure 7: Soil column geometry and mesh.*

382

383 *Figure 8: Aldicarb reaction chain.*

384 The simulation time is 8 days with a splitting time step of 0.05 days. The number of nodes is
385 3936 nodes. Figure 9a and Figure 9b show the concentration in the soil column of Aldicarb
386 and Aldicarb sulfone, respectively. Aldicarb disappears fast from the domain since its kinetic
387 constant are fast in comparison to the kinetic constants of the daughter species. Therefore,
388 Aldicarb (and also Aldicarb oxime) are presented close to the infiltration condition. On the
389 contrary, the other daughter species (Aldicarb sulfoxide, aldicarb sulfone, aldicarb sulfoxide
390 oxime, aldicarb sulfone oxime) have a similar distribution in the domain. Figure 9c and 9d
391 show the concentration of Aldicarb and Aldicarb sulfone when $r = 0$ m for the different OS
392 methods and COMSOL alone. It is possible to see a good agreement between all the methods,
393 although a discrepancy between the methods and COMSOL is observable. The discrepancy is
394 related to the OS error and the chosen integration time scheme for the chemistry step.



395 *Figure 9: a) Aldicarb contour plot after 8 days, b) Aldicarb oxime contour plot after 8 days,*
 396 *c) Concentration aldicarb at $r = 0$ m for all the methods and Comsol, d) Concentration*
 397 *aldicarb oxime at $r = 0$ m for all the methods and Comsol.*

398 5. Discussion

399 As shown by many previous studies and by the four examples of the previous section, reactive
 400 transport problems can be solved by a wide diversity of transport, chemistry, and operator
 401 splitting methods. No method is currently accepted as systematically more accurate and
 402 efficient than any other. Integration of the transport and chemistry operators in PHREEQC
 403 using more appropriate splitting with advection-reaction on one side and diffusion-reaction on

404 the other side leads to better resolution of chemical fronts as shown in the second and third
405 cases (Parkhurst and Appelo, 1999), but such front can be obtained by smaller time steps. It is
406 not only the integration but also the successive improvements of the methods that lead to
407 significantly more accurate schemes. TReacLab results remain however close, displaying the
408 same overall behavior both on solute and mineral concentrations. The interest of fully
409 segmented reactive transport implementations like in TReacLab is not motivated by the
410 accuracy and should not be used when other more integrated and optimized software are
411 appropriate and freely available.

412 Despite their lower accuracy, fully segmented implementations may be useful in situations
413 where flexibility is essential. It is the case when extensive modeling work has been performed
414 in independent software environments for transport or chemistry, and extensions to reactive
415 transport problems are required. Transport and chemistry solvers are then imposed and should
416 be coupled with as few specific developments as possible. For example, COMSOL and
417 PHREEQC have been interfaced here and in several other works because of their
418 complementarity (Nardi *et al.*, 2014; Nasir *et al.*, 2014; Wissmeier and Barry, 2011). It is
419 possible to specify advanced geometrical configurations in COMSOL through a convenient
420 graphical user interface (Azad *et al.*, 2016). PHREEQC provides advanced capacities for
421 modeling complex geochemical systems with extensive database of reactions (Charlton and
422 Parkhurst, 2011; Parkhurst and Wissmeier, 2015). In such cases, building the structure of the
423 model may be the first and dominant issue in developing simulation capacities. That is when
424 codes like TReacLab can provide practical bridges for reactive transport systems. The
425 examples of section 4 however shows that they must be used with great care. Especially, the
426 called software may have different temporal integration schemes than the explicit and implicit
427 methods required by the SNIA and SIA coupling methods as discussed for the higher-order
428 schemes of COMSOL in section 4. Using codes like COMSOL may enhance robustness at a

429 certain cost of accuracy. Thus, implementation capacity does not guarantee validity. Validity
430 must be carefully checked and argued with other comparable cases or with appropriate
431 convergence analysis.

432 Another targeted use of TReacLab concerns the development and test of new coupling
433 methods or strategies. Operator splitting can be performed with various methods including for
434 example adaptative time stepping (Belfort *et al.*, 2007; Gasda *et al.*, 2011). Global implicit
435 approaches that separate geochemical and transport software might also be more widely tested
436 providing the Jacobian of the chemical operator and taking into account current limitations
437 such as the difficulties to model precipitation/dissolution reactions (Amir and Kern, 2010).
438 TReacLab may then be used as a platform where interfaces to chemical and transport
439 operators are available and have been tested and documented for other coupling methods.

440 These applications are possible because TReacLab is a fully free and open software that can
441 be directly accessed and downloaded (<https://github.com/TReacLab/TReacLab>). The free and
442 open use of TReacLab has been dominant in its development and in the choices made for its
443 organization. The repository thus provides two main directories with sources and examples
444 respectively. Sources are organized in four main categories for chemistry, transport, coupler
445 and utilities. At the root of the chemistry, transport and coupler directories are the virtual
446 classes as main entries. Examples of instantiations are provided in the subdirectories.
447 Additional developments may take advantage of the documented examples provided at the
448 different levels of the software.

449 **6. Conclusion**

450 We provide in the TReacLab code a fully segmented implementation of the coupling of
451 independent geochemical and transport software. Coupling is based on a general expression of

452 the split-operator strategy with a set of classical methods. TReacLab should facilitate the
 453 development of reactive transport simulation capacities for independent reactive and transport
 454 software. Systematic comparison to the well-established PHREEQC model for uniform 1D
 455 reactive transport cases shows a good agreement with TReacLab. Systematic comparison
 456 against COMSOL for the 2D problem shows that full decoupling at the implementation level
 457 has a cost in accuracy. Sharp dissolution fronts of thermodynamically controlled reactions
 458 especially are generally smoothed in split-operator strategies. Steeper fronts might be
 459 recovered with smaller splitting time steps at larger computational costs. Beyond the
 460 implementation and the simulation capacity, consistency and validity of the numerical models
 461 should be systematically assessed. TReacLab can be freely accessed and used to promote the
 462 development of coupling methods and to provide additional modeling capacity for reactive
 463 transport coupling in geological media.

464 **Appendix A: Implemented operator splitting methods**

465 We detail the mathematical formulation for the sequential splitting (Geiser, 2009) :

$$\frac{\partial Z^1}{\partial t} = \mathcal{L}_1 Z^1, \quad Z^1(x, t^n) = Z(x, t^n), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.1})$$

$$\frac{\partial Z^2}{\partial t} = \mathcal{L}_2 Z^2, \quad Z^2(x, t^n) = Z^1(x, t^{n+1}), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.2})$$

$$Z(x, t^{n+1}) = Z^2(x, t^{n+1}), \quad (\text{A.3})$$

466 the additive splitting (Faragó *et al.*, 2008a; Faragó *et al.*, 2008b) :

$$\frac{\partial Z^1}{\partial t} = \mathcal{L}_1 Z^1, \quad Z^1(x, t^n) = Z(x, t^n), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.4})$$

$$\frac{\partial Z^2}{\partial t} = \mathcal{L}_2 Z^2, \quad Z^2(x, t^n) = Z(x, t^n), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.5})$$

$$Z(x, t^{n+1}) = Z^1(x, t^{n+1}) + Z^2(x, t^{n+1}) - Z(x, t^n), \quad (\text{A.6})$$

467 the Strang splitting (Strang, 1968) :

$$\frac{\partial Z^1}{\partial t} = \mathcal{L}_1 Z^1, \quad Z^1(x, t^n) = Z(x, t^n), \quad t^n \leq t \leq t^{n+1/2}, \quad (\text{A.7})$$

$$\frac{\partial Z^2}{\partial t} = \mathcal{L}_2 Z^2, \quad Z^2(x, t^n) = Z^1(x, t^{n+1/2}), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.8})$$

$$\frac{\partial Z^1}{\partial t} = \mathcal{L}_1 Z^1, \quad Z^1(x, t^{n+1/2}) = Z^2(x, t^{n+1}), \quad t^{n+1/2} \leq t \leq t^{n+1}, \quad (\text{A.9})$$

$$Z(x, t^{n+1}) = Z^1(x, t^{n+1}), \quad (\text{A.10})$$

468 and the symmetrically weighted splitting (SWS) (Csomós *et al.*, 2005) :

$$\frac{\partial Z^1}{\partial t} = \mathcal{L}_1 Z^1, \quad Z^1(x, t^n) = Z(x, t^n), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.11})$$

$$\frac{\partial Z^2}{\partial t} = \mathcal{L}_2 Z^2, \quad Z^2(x, t^n) = Z^1(x, t^{n+1}), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.12})$$

$$\frac{\partial Z^{2*}}{\partial t} = \mathcal{L}_2 Z^{2*}, \quad Z^{2*}(x, t^n) = Z(x, t^n), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.13})$$

$$\frac{\partial Z^{1*}}{\partial t} = \mathcal{L}_1 Z^{1*}, \quad Z^{1*}(x, t^n) = Z^{2*}(x, t^{n+1}), \quad t^n \leq t \leq t^{n+1}, \quad (\text{A.14})$$

$$Z(x, t^{n+1}) = \frac{Z^2(x, t^{n+1}) + Z^{1*}(x, t^{n+1})}{2}. \quad (\text{A.15})$$

469 The alternating splitting algorithm (Valocchi and Malmstead, 1992) is based on a sequential
 470 splitting. It is defined by two successive splitting time steps with a permutation of the operator
 471 sequence between the splitting time steps.

472 **Appendix B: Complementary notes on software organization**

473 We successively describe the general toolbox organization, the coupler, transport and
 474 chemistry classes. We concretely show how operator splitting methods can be introduced and
 475 how other transport and geochemical codes can be connected.

476 **B.1 Coupling methods**

477 The coupler is at the center of TReacLab as it performs the temporal integration and calls the
 478 transport and chemistry solvers through the OS algorithm. In the pre-processing phase, it gets
 479 the initial conditions and the temporal constraints of the integration. It is also in charge of

480 storing the required results before formatting and outputting them in the post-processing
481 phase. Because the coupler is at the core of the toolbox, its methods remain generic.
482 Interactions with the transport and chemistry solvers are also fully generic thanks to template
483 interfaces calling external software and managing the exchange of information. Calling
484 external software relies on the so-called `Solve_Engine` method for both transport and
485 chemistry software. `Solve_Engine` takes as inputs the concentration data and the time step
486 over which the integration must be performed. It returns the updated concentrations, a flag to
487 check the success of the integration and an error message in case of failure to activate and
488 inform the error management procedure mentioned in the former section. The coupler is based
489 on a fixed structure of concentration data. Whatever the structure of concentrations in the
490 transport and chemical codes, the structure of concentrations within the coupler is always the
491 same. It consists in a matrix with in columns chemical species and in rows the position within
492 the domain (Figure B.1). The size of the matrix is equal to the number of cells times the
493 number of chemical species and components passed through the coupler. Chemical species
494 include solutes and fixed species. As this is the sole link between the chemical code and the
495 coupler also in charge of temporary results storage for the post-processing, it must transfer all
496 quantities necessary for the algorithm and for the later extraction. The format of the matrix is
497 set in the pre-processing phase and it is fixed for the whole simulation. TReacLab does not
498 support yet any modification of species number to transfer between codes. Even if some
499 solute species are absent over some time of the simulation, they will be transferred. This
500 choice does not limit the capacity of the software as long as the chemical system is known
501 from the beginning but might have some consequences on its performance in cases where
502 solute composition strongly evolves. The choice of generality and flexibility, here like in
503 other places, has a cost in efficiency. All modifications of concentration format are eventually
504 performed in the interfaces between the coupler and the transport and chemistry solvers

505 (Figure 1).

Domain id	C	Mg	Calcite	Dolomite
1	$2 \cdot 10^{-4}$	$7 \cdot 10^{-2}$	0.7	2
2	$1 \cdot 10^{-4}$	$8 \cdot 10^{-2}$	0.6	2.1
...
n	$1 \cdot 10^{-4}$	$9 \cdot 10^{-2}$	0.6	3

506

507 *Figure B.1: Concentration format internal to the coupler class. To ensure generality, this*
 508 *structure of concentration is always the same and does not depend on the external transport*
 509 *and chemistry software. Species concentration are given in columns and are passed to the*
 510 *transport software as such. Concentrations at given locations are stored in rows with both*
 511 *mobile and fixed species. They are transferred either line per line or globally to the chemistry*
 512 *software. Fixed species are transferred from the chemistry code to the coupler to enable their*
 513 *possible use in the post-processing phase for results and outputs.*

514 Thanks to the template methods calling the transport and chemical solvers and to the generic
 515 concentration format, operator splitting methods can be simply implemented. These are not
 516 more than a combination of simple calls of solvers passing and updating concentration
 517 information. Several sequential non-iterative techniques have thus been implemented, as
 518 detailed in section 2.3.

519 Specifications of the coupler are thus the name of the coupling method necessary to switch to
520 the corresponding method in the coupler class, the temporal constrains of the integration and a
521 vector of additional parameters. Temporal constrains of the integration are not only the initial
522 and final times of the integration but also the times at which the solution must be stored. All
523 time related parameters are stored into a time class. Additional parameters may be tolerances
524 for example when using sequential iterative approaches. Instantiation of the coupler class thus
525 consists in providing the identifier of the chosen coupling technique, the time constrains in the
526 time class (initial time, final time, time to save the results, OS time step) and the additional
527 parameters possibly needed by the algorithm.

528 **B.2 Geochemical solver**

529 Geochemical codes widely differ by their principles, the type of reactivity they consider and
530 their input/output formats and parameters. We propose to normalize some of their interface to
531 simplify exchanges with the coupler. In any case of equilibrium or kinetic reactions or of a
532 mixed combination of them, geochemical codes steadily take concentrations, reaction
533 constants, rate parameters, reaction times, as inputs and return output concentrations. All
534 specifications linked to the choice of components, primary and secondary species should be
535 set in the geochemical code or in the interface so that the geochemical solver does not have to
536 be modified and the coupler remains generic. Whether components are used or not, the
537 definition of the chemical system is not unique. Even when components are used, several
538 alternative and reliable definitions can be chosen (Fang *et al.*, 2003; Hoffmann *et al.*, 2012;
539 Molins *et al.*, 2004). Numerical and conceptual consistencies between the transport and
540 chemical systems should thus be ensured externally before any implementation.

541 While solute concentrations are instantiated by the coupler and systematically passed to the
542 geochemical solver, equilibrium and kinetic constants are considered as constant. They are

543 defined once for all in the pre-processing phase. For example in PHREEQC, chemical
544 reactions and constants are already defined in databases like 'Phreeqc.dat' or 'lnl.dat'.
545 Initialization of mineral quantities is done at the beginning of the simulation when setting the
546 initial conditions through the coupler. The interface between the coupler and the geochemical
547 solver is made up of the Solve_Engine that calls the geochemical solver and the methods that
548 modify the concentration format. By default, the geochemical solver is instantiated and stored
549 for each of the nodes of the computational grid for the whole domain of the simulation. Any
550 data that are not passed to the coupler is, in general, kept in the instances of the geochemical
551 code. Another option is provided by software that allow simultaneous computations for
552 several independent batches like it is for example the case of PHREEQC. In such cases only
553 one instance of the geochemical solver is necessary. Exchanges of data between the coupler
554 and the geochemical solver are defined in the pre-processing phase and remain fixed for the
555 whole duration of the simulation. It is precisely at this stage that components are derived
556 through the algebraic operations of equation (6) and passed to the coupler. The coupler does
557 not manage the transformation of concentration and species but just their transfer between the
558 transport and geochemical solvers. The use of components does not fundamentally change the
559 calling sequence of the geochemical operator but modifies its interface to the coupler.
560 Components may be specified by the geochemical code like in PHREEQC or by the user in
561 the pre-processing phase by loading the matrix of U (equation (6)). In this latter case,
562 components are defined by the user in the pre-processing phase and are computed by the
563 interface that adapts the information to be passed through the coupler to the transport solver.

564 Connection of a new geochemical code requires essentially four operations. First, a new
565 daughter class of the template chemistry class must be defined. It can be built up using, as
566 template, one of the examples provided and described in the section 4. Second, an interface
567 must be created to filter the required information given from the coupler to the Solve_Engine

568 method. Third, an instantiation procedure should be provided whether it is internal or external
569 to TReacLab. Fourth, the template Solve_Engine calling function of the geochemical solver
570 must be written and optionally tested before being effectively used in reactive transport
571 problems.

572 **B.3 Transport solver**

573 Despite the diversity of the transport mechanisms and numerical schemes to solve them, we
574 provide here a basic interface designed mostly to address transport in a generic way. As
575 previously stated, this approach assumes that transport parameters are not modified by the
576 species concentration. This absence of feedback currently precludes density driven flows as
577 well as permeability and porosity modifications due to precipitation or dissolution. TReacLab
578 might be extended in this direction on the basis of slow evolutions of porosity or density. The
579 transport operator relies on concentration independent parameters. We detail in the following
580 the interaction between the coupler and the transport classes with the exchange of data and the
581 instantiation of the transport solver. We will conclude this section with the development
582 required to connect other transport codes.

583 While geochemical codes operate on species concentration on a given computational node,
584 transport codes operate on a given species concentration over all the domain. In terms of data
585 structure, each of the columns of the concentration array are successively transferred to the
586 geochemical code and each of the rows (or linear combinations of rows) are given to the
587 transport code (Figure B.1). The transport operator is thus iteratively called for each of the
588 species or components explicitly specified in the interface between the coupler and the
589 transport solver (Figure 1). The time range over which temporal integration should be
590 performed and the identifiers of the transported species are also transferred to the transport
591 solver. Species identification is essential when considering species sensitive diffusion

592 coefficient. The transport solver returns the updated concentration field at the final time of the
593 time range, an indicator of success or failure of the integration and a message to document
594 algorithm failures. The basic exchange of concentrations with the imposed integration times
595 are the sole requirements for the coupler to proceed.

596 All other parameters of the transport code should be set in the pre-processing phase, which
597 may become an important part of the eventual reactive transport code. In fact it does not cover
598 only the flow and transport parameters but more broadly the full structure of the domain, of
599 the computational grid, and of the boundary conditions. As for the geochemical code, the
600 transport code can be instantiated internally or externally. In case of internal definition, it
601 should contain at least the flow and transport properties, the morphology of the domain and
602 the structure of the computational grid (coordinates of the computational nodes). A default set
603 of classes is provided for 1D problems as templates for the morphology (domain definitions),
604 the computational grid (identification and coordinates of nodes and edges), the boundary
605 conditions (nature and values for boundary conditions) and the hydraulic and transport
606 properties. We recall as also said in section 2.2 that some operator splitting techniques might
607 impose limitations on the transport solver in terms of integration scheme or in terms of time
608 step (de Dieuleveult *et al.*, 2009). Both the OS technique and the transport integration should
609 be chosen consistent.

610 Operations on the transport class are thus decomposed between the pre-processing and the
611 processing phases. Specifications of the operator with all necessary parameters is performed
612 in the pre-processing phase. Only generic exchanges of concentrations are needed in the
613 processing phase. Additional information would generally be needed externally to identify the
614 location of the computational nodes. More advanced information from the definition of the
615 domain, parameters and boundary conditions will be generally defined in the transport code

616 rather than in TReacLab. For example, Comsol or Modflow have their own grid definitions.
617 They are complete and efficient. It may be straightforwardly extracted and cross-referenced
618 with the results of TReacLab as long as the cell numbers correspond, a basic but necessary
619 requirement. This choice is motivated by both the generality and the simplicity of TReacLab.
620 It also highlights that TReacLab remains a coupler that transfers information and does not
621 process in any way the relation of concentrations between cells like a transport operator does.

622 The methodological choice of handling the spatial dimension of the problem within the
623 transport operator is not only operational. It is also ensuring the capacity to connect a wide
624 range of transport codes with their own logic and structure. For example, the multi-physics
625 software COMSOL has its own mesh generator methods and internal structures that should
626 not be duplicated in TReacLab but interfaced. Connecting other codes would thus require
627 reduced work as long as they can already be called from the same environment of
628 development (here MATLAB) on a discretized time basis. More in details, any new transport
629 code would require: 1) the development of the main calling function Solve_Engine to call it
630 from the coupler 2) the adaptation of the concentration format in the interface methods that
631 match the concentrations to the internal data structure of the external code, 3) the instantiation
632 of the transport class and 4) the access to the coordinates of the computational nodes for
633 outputs purposes. As for the geochemical code, implementation of the interface should be
634 checked before any full reactive transport coupling. This can be completed within TReacLab
635 by using an idle process instead of the geochemical code.

636 **Acknowledgements:** We acknowledge ANDRA and the ANR project H2MNO4 under the
637 number ANR-12-MONU0012-01 for their financial support, Jocelyne Erhel and David L.
638 Parkhurst for constant and fruitful discussions, and Javier Molinero for initial exchanges.

639

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- 853

Highlights

- Object-oriented implementation of non-intrusive couplings for reactive transport
- Validation for 3 equilibrium and kinetically controlled 1D cases with PhreeqC and one 2D case with COMSOL.
- Illustration of implementation flexibility with different transport and reaction codes