

1 PROOST: Object oriented approach to multiphase reactive transport 2 modeling in porous media.

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12 13 **Abstract**

14 Reactive transport modelling involves solving several nonlinear coupled phenomena, among
15 them, the flow of fluid phases, the transport of chemical species and energy, and chemical
16 reactions.. There are different ways to account this coupling that might be more or less
17 suitable depending on the nature of the problem to be solved. In this paper we acknowledge
18 the importance of flexibility on reactive transport codes and how object oriented programming
19 can facilitate this feature. We present PROOST, an object oriented code that allows solving
20 reactive transport problems considering different coupling approaches. The code main classes
21 and their interactions are presented. PROOST performance is illustrated by the resolution of a
22 multiphase reactive transport problem where geochemistry affects hydrodynamic processes.

23 24 **1. Introduction**

25 Reactive transport models are tools that help to understand the hydraulic and chemical
26 behavior of natural and artificial porous media. It has been used to solve a broad range of

27 problems like groundwater remediation (Loomer et al. 2010), nuclear waste disposal
28 (MacQuarrie and Mayer 2005) and CO₂ sequestration (Zhang et al. 2012) among others, from
29 micro scale (Trebortich et al. 2014) to field scale problems (Sassen et al. 2012).

30 Modeling reactive transport in porous media involves simulating several coupled phenomena:
31 phase flow, solute transport, and reactions. It may also involve multiphase flow, heat transport
32 and porous media deformation (Steefel et al. 2014,). These phenomena may be complex to
33 model individually, and modeling together brings on new difficulties associated with coupled
34 effects (Lichtner 1996). Which coupled effects have to be considered and the optimal solution
35 strategy for the coupled equations depend on the nature of the problem to be solved and may
36 vary significantly from case to case (Zhang et al. 2012).

37 The ideal reactive transport code would have to use an accurate, robust and efficient
38 numerical approach. However, it is difficult to obtain these goals with a single numerical
39 approach. Therefore, concessions have to be made and different coupling alternatives have to
40 be chosen at different levels. Numerical accuracy is generally preferred on other issues when
41 solving modeling research applications. On the other hand, when solving field scale problems,
42 efficiency and robustness have priority while accuracy remains within the bounds of the
43 uncertainty associated with model parameters (Yeh et al. 2012).

44 Two big family of methods were addressed to account for the coupling between solute
45 transport and chemical reaction processes: (1) the Operator Splitting (or Sequential Iterative
46 (or NON-iterative) Approach, and (2) the Global Implicit or Direct Substitution Approach
47 (Saaltink et al. 2001). As regards the first one (i.e., the sequential methods), whether iterative
48 (SIA) or not (SNIA) adopt operator splitting techniques that effectively decouple component
49 transport equations. As regards the last one, direct substitution approaches (DSA) solve both
50 transport and chemical reactions simultaneously. A number of authors have studied the
51 numerical performance of these methods (Steefel and MacQuarrie, 1996), and they conclude
52 that in spite of the fact that the DSA is more accurate and robust, there are cases where the

53 SIA is more convenient from an efficiency-accuracy point of view. In addition, SNIA may be
54 appropriated for scenario with Courant number smaller than 1 (Xu et al. 2012). Some reactive
55 transport codes are able to work with both of these approaches (CRUNCHFLOW, Steefel 2009;
56 DUMUX, Flemisch et al. 2011; HYDROGEOCHEM, Yeh et al, 2010; PFLOTRAN, Lichtner et al.
57 2013; RETRASOCODEBRIGHT et al. Saaltink et al. 2004.), while others use the fully implicit
58 approach (NUFT, Hao et al. 2012; MIN3P, Mayer et al. 2012), or different variants of operator
59 splitting techniques (CORE, Samper et al 2009; HYDRUS-PHREEQC (HP1), Jacques et al. 2011;
60 HYTEC, Lagneau and Van Der Lee 2010; IPARS, Wheeler et al. 2012; OPENGEOLOGY, Li et al. 2014;
61 ORCHESTRA, Meeussen 2003; PHAST, Parkhurst et al. 2010; PHREEQC, Parkhurst and Appelo
62 2013; PHT3D, Prommer and Post 2010; RT3D, Johnson and Truex 2006; STOMP, White and
63 McGrail 2005; TOUGHREACT, Xu et al. 2011).

64 On a more complex level is the coupling between phase conservation and reactive solute
65 transport. Most reactive transport codes decouple phase conservation (i.e. flow equation)
66 from reactive transport calculations (RT3D, MIN3P, PFLOTRAN, PHAST, RETRASOCODEBRIGHT,
67 HYTEC, TOUGHREACT).

68 This approach is convenient in most cases, but a numerically coupled solution will generally be
69 more suitable when the phenomena involved are highly physically coupled. One example of
70 this could be found in problems related with the CO₂ sequestration in brine aquifers, which has
71 prompted the development of codes that solve coupled multiphase flow and reactive
72 transport (Fan et al. 2012) and even mechanical deformation (Zhang et al. 2012). Likewise,
73 Wissmeier and Barry (2008) showed that the consumption of water due to hydrated mineral
74 precipitation can have impacts on flow and solute transport for unsaturated flow problems.
75 These impacts can be even more important if gas transport is also considered because water
76 activity, which controls vapor pressure, is affected by capillary and osmotic effects. Moreover,
77 certain mineral paragenesis can fix water activity (producing an invariant point), causing the
78 geochemistry to control vapor pressure, which is the key variable for vapor flow (Risacher and

79 Clement, 2001). In such cases, decoupling is not appropriated. Formulations that are able to
 80 represent these effects are complex to implement since they should consider all coupled
 81 phenomenon and a variable number of components in space and time.

82 While most reactive transport codes consider a single technic for the resolution of the partial
 83 differential equation some codes can adopt more than one. In Table 1 the supported
 84 discretization method and coupling strategies for different reactive transport codes are
 85 detailed.

86 Table 1 – Supported discretization method and coupling strategies for different reactive transport codes

Code	PDE discretization ¹	Transport and reaction coupling ²	Phase conservation and transport coupling ³
CORE	FEM	OS	SEQ
CRUNCHFLOW	FVM	OS, DS	COU
DUMUX	FEM, FVM, MFDM	OS, DS	COU, SEQ
HYDROGEOCHEM	FEM, MMC	OS, DS	ITER
HYDRUS-PHREEQC (HP1)	FEM	OS	SEQ
HYTEC	FVM	OS	SEQ
IPARS	MFEM, DGM	OS	INDP
NUFT	FVM	DS	SEQ
MIN3P	FVM	DS	SEQ
OPENGEOSYS	FEM	OS	SEQ
ORCHESTRA	MC	OS	INDP
PFLOTRAN	FVM	OS, DS	SEQ
PHAST	FDM	OS	INDP
PHREEQC	MC	OS	INDP
PHT3D	FVM, MMC	OS	INDP
RETRASOCODEBRIGHT	FEM	OS, DS	SEQ, ITER
RT3D	FDM	OS	INDP
STOMP	FEM	OS	SEQ
TOUGHREACT	FVM	OS	SEQ

¹ DGM Discontinuous Galerkin Method, FDM Finite Difference Method, FEM Finite Elements Method, FVM Finite Volume Method, MC Mixing Cell, MFDM Mimetic Finite Difference Method, MFEM Mixed Finite Element Method, MMC Modified Method of Characteristic

² DS Direct Substitution, OS Operator Split

³ COU Coupled, INDP Independent, ITER iterative, SEQ sequentially

87

88 Reactive transport modeling in fractured media might also require flexibility regarding the way
 89 the medium is considered. Important changes in fluid pressures and solute concentrations will
 90 propagate rapidly through the fracture system, while exchanges with the matrix blocks will

91 occur slowly. To account this, some reactive transport codes have included Multiple
92 Interacting Continua modeling (TOUGHREACT, PFLOTRAN).

93 In short, for reactive transport modeling the adopted coupling techniques, the partial
94 differential equation discretization method and the way as the domain is considered, may be
95 problem dependent. Therefore, a reactive transport code should include several solution
96 approaches to be used in a broad range of problems. Moreover, in order to ensure its use for
97 present and future problems, it must have an extensible design. A number of authors have
98 pointed out that object oriented (OO) programming facilitates the implementation of these
99 features (Commend and Zimmermann 2001, Filho and Devloo 1991).

100 The scientific community has been adopting OO techniques for problem solving since the end
101 of the last century (Forde et al. 1990, Slooten et al. 2010, Wang and Kolditz 2007). But only in
102 the last decade have OO codes been developed for reactive transport modeling. Meysman et
103 al. (2003) developed an OO reactive transport code for a single fluid phase. Gandy and
104 Younger (2007) developed an OO multiphase reactive transport code for pyrite oxidation and
105 pollutant transport in tailing ponds. Shao et al. (2009) include reactive transport calculations
106 into a Thermo-Hydro-Mechanic OO framework adopting a sequential non iterative approach
107 (SNIA). Bea et al. (2009) developed an OO module capable of solving reactive transport for a
108 single phase considering the SNIA, SIA or DSA approach. However, all of these codes, and most
109 of the procedural reactive transport codes, have a predefined strategy for dealing with
110 coupling effects. Particularly, they do not allow for changing number and definitions of
111 chemical components when solving flow and reactive transport in a coupled way.

112 The objective of this paper is to present an OO structure for reactive transport that can
113 accommodate different level of physical and chemical processes coupling. The structure
114 presented here is capable to model from single-phase SIA problems to fully coupled
115 multiphase reactive transport problems. In addition, the best of our knowledge, it is the first
116 OO tool capable to account the occurrence of invariant points (e.g., for reference see Risacher

117 and Clement) in a reactive transport problem. This is an extreme case where geochemical
118 processes significantly affect fluid flow and the number and definitions of chemical
119 components may vary significantly in space and time. This structure has been implemented in
120 PROOST which was programmed in FORTRAN 95 following the OO paradigm, and until now
121 could solve single phase reactive transport by the SIA method and a fully coupled multi-phase
122 reactive transport by the DSA method.

123

124 **2. Equations to solve**

125 Reactive transport modeling implies establishing several conservation principles, like mass or
126 energy conservation, expressed as partial differential equations (PDE), and several constitutive
127 and thermodynamic laws (such as retention curve or mass actions laws) expressed as algebraic
128 equations (AE). Darcy's law is used to represent momentum conservation. In this section we
129 present a generic conservation equation to represent conservation principles in reactive
130 transport problems. We consider in detail the species and component conservation and we
131 briefly present the constitutive and thermodynamic laws.

132 2.1. General conservation equation

133 Conservation of a physical entity ε can be expressed as

$$134 \quad \frac{\partial A_\varepsilon}{\partial t} = - \sum_\nu \nabla \mathbf{j}_{\varepsilon,\nu} + F_\varepsilon \quad (1)$$

135 Where A_ε is the amount of ε per unit volume of medium, $\mathbf{j}_{\varepsilon,\nu}$ is the flux of ε due to the
136 driving force ν (e.g. advection or diffusion), and F_ε is a sink source term. Since time and spatial
137 derivatives are involved, conservation equations usually take the form of a partial differential
138 equation (PDE).

139 2.2. Species and component conservation equation

140 The conservation of a species i belonging to phase α , which is a particular case of equation
 141 (1) has the following expression:

$$142 \quad \frac{\partial}{\partial t}(\theta_\alpha c_{i,\alpha}) = L_\alpha(c_{i,\alpha}) + \sum_{j=1}^{Ne} Se_{j,i} \cdot re_j + \sum_{j=1}^{Nk} Sk_{j,i} \cdot rk_j + f_i \quad (2)$$

143 Where θ_α is the volumetric content of phase α , $c_{i,\alpha}$ is the species i concentration in α
 144 phase, $Se_{j,i}$ is the stoichiometric coefficient of the equilibrium reaction j for the specie i ,
 145 re_j is the reaction rate of the equilibrium reaction j , and Ne is the number of equilibrium
 146 reactions. $Sk_{j,i}$, rk_j and Nk are analogous to $Se_{j,i}$, re_j and Ne but for kinetic reactions. f_i is
 147 an external sink-source term, and $L_\alpha(\)$ is the linear transport operator for the mobile phase
 148 α involving advective and diffusive-dispersive processes:

$$149 \quad L_\alpha(c_{i,\alpha}) = -\nabla \cdot (c_{i,\alpha} \mathbf{q}_\alpha) - \nabla \cdot (\mathbf{j}_{D_\alpha,i}) \quad (3)$$

150 Mobile phase fluxes \mathbf{q}_α are calculated according to Darcy's law:

$$151 \quad \mathbf{q}_\alpha = \mathbf{K}_\alpha (-\nabla p_\alpha + \rho_\alpha \mathbf{g}) \quad (4)$$

152 where \mathbf{K}_α , p_α and ρ_α are the conductivity tensor, pressure and density of the phase α
 153 respectively. Diffusive-dispersive fluxes $\mathbf{j}_{D_\alpha,i}$ are calculated according to Fick's law:

$$154 \quad \mathbf{j}_{D_\alpha,i} = -\mathbf{D}_\alpha \cdot \nabla(c_{i,\alpha}) = -(\mathbf{D}_\alpha^{diff} \theta_\alpha \tau + \mathbf{D}^{disp}) \cdot \nabla(c_{i,\alpha}) \quad (5)$$

155 where \mathbf{D}_α^{diff} and \mathbf{D}^{disp} are the diffusion and dispersion tensor for phase α respectively and τ is
 156 the tortuosity.

157 Note that the general sink source term of equation (1) F_ε involves several different terms in
 158 equation (2):

$$159 \quad F_\varepsilon = \sum_{j=1}^{Ne} Se_{j,i} \cdot re_j + \sum_{j=1}^{Nk} Sk_{j,i} \cdot rk_j + f_i \quad (6)$$

160 There is no explicit expression for the equilibrium reaction rates re_j , their value has to be such
 161 that the corresponding mass action law is satisfied. Therefore, re_j values can be written as a
 162 function of both transport and chemical processes (De Simoni et al. 2005). A common
 163 approach to avoid dealing with these terms is to formulate the conservation of components as
 164 a linear combination of species that remain unaffected by equilibrium reactions. As such,
 165 equilibrium reactive rates disappear from the conservation equations of components (Steeffel
 166 and MacQuarrie 1996). However, components may involve species belonging to different
 167 phases, therefore conservation equation for components have to be written:

$$168 \quad \sum_{\alpha} \frac{\partial}{\partial t} (\theta_{\alpha} u_{i,\alpha}) + \sum_{\beta} \frac{\partial}{\partial t} (\theta_{\beta} u_{i,\beta}) = \sum_{\alpha} L_{\alpha} (u_{i,\alpha}) + k_{u_i} + f_{u_i} \quad (7)$$

169 Where $u_{i,\alpha}$ and $u_{i,\beta}$ are the i component concentration in mobile phases α and immobile
 170 phases β respectively, and k_{u_i} is a linear combination of the kinetic terms that affect the
 171 species composing the component. We consider as immobile phases minerals and fluid-solid
 172 interface, despite the fact an interphase is not a phase from a thermodynamic point of view.
 173 Note that the component conservation equation (7) has the same structure as equation (2).
 174 The main difference is that a component u_i may be present in more than one phase, while a
 175 species c_i belongs to a single phase. There are several ways of defining components and
 176 therefore some freedom in the choice of components. This has led to formulations that try
 177 defining components that do not affect each other, such as those proposed by Molins et al.
 178 (2004), Krättele and Knabner (2005) and Hoffmann et al. (2010). Saaltink et al. (1998)
 179 introduced a definition that eliminates species whose activities are known and constant. That
 180 is the case of minerals, that are considered as pure phases, so that their activity equals unity.
 181 Also, the activity of water can be assumed unity for the case of diluted solutions. Minerals,
 182 often considered as constant activity species, might appear or disappear from portions of the
 183 domain due to precipitation-dissolution processes. Therefore, under equilibrium assumption,

184 the dimension of the component vector, the number of components, may be different at each
185 discrete point in space and vary in time. This increases the difficulty of solving equation (7)
186 since the matrix system to be solved has a dynamic size, which significantly affects the code.
187 Once all component conservation and geochemical equations have been solved, all species
188 concentrations are known. Equilibrium reaction rates re_j are then calculated from species
189 conservation equation (2). If constant activity species have been eliminated from the
190 component definition, their concentration must also to be calculated from equation (2).

191

192 2.3. Constitutive and thermodynamic laws

193 The literature provides several models for density, viscosity and diffusion coefficients of mobile
194 phases. These parameters are usually expressed as an explicit function of phase composition,
195 pressure and temperature. Several models express saturation and relative permeability as an
196 explicit function of capillary pressure and surface tension. All these relations lead to a local
197 system of equations, which is valid at every point of the domain.

198 Thermodynamic relations also form part of this local system of equations. The most important
199 of these are the chemical equilibrium reactions, which may be expressed by means of mass
200 action laws, as often done in reactive transport. Also required are models for the calculation of
201 activity, such as Debye-Hückel (1923), or Pitzer (1973) and expressions for kinetic rate laws
202 (such as Monod or Lasaga, Mayer et al. 2002).

203 Minor changes on the solid matrix, like porosity changes due to mineral dissolution-
204 precipitation or clogging, may also be expressed as algebraic equations (Soleimani et al. 2009).

205 More complex mechanical processes, like deformation or consolidation, involve momentum
206 conservation equation and have to be solved as a PDE (Villar et al. 2008).

207 Constitutive and thermodynamic relationships define a set of algebraic equations (AE) that
208 have to be solved together with the conservation equations (PDE).

209

210 2.4. Numerical solution of the equations

211 Methods such as finite element or finite differences, among others, are normally used to
212 approximate time or space derivative terms in PDEs. Application of such methods leads to a set
213 of equations that represent the conservation principle for discrete portions of the domain
214 (representing nodes or cells). The current version of PROOST supports two methods: the Finite
215 Elements and the Mixed Finite Elements. Contrary to constitutive or thermodynamic laws,
216 these equations are not local, that is, equations at a discrete point are function of variables at
217 other discrete points. As constitutive and thermodynamic models (AEs) involve variables that
218 appear in the PDE, both AEs and PDEs may have to be solved simultaneously. Generally, the
219 resulting set of equations is non-linear, which makes their solution more difficult. As
220 mentioned in the introduction different approaches can be adopted for solving these coupled
221 sets of equation: independently, sequentially, iteratively or coupled.

222

223 **3. OO analysis of reactive transport modeling and PROOST class organization**

224 According to the OO philosophy, the numerical solution of reactive transport can be
225 represented by a group of interacting objects. These objects belong to classes which define
226 common types of data and functionality. According to Filho and Devloo (1991), defining
227 suitable classes is the first and perhaps the most important step in software design under OO.

228 Our analysis was based on the following abstraction: reactive transport modeling is considered
229 as a set of equations (PDEs and AEs), representing the conservation of chemical species, that
230 need to be solved in a certain domain. These equations involve several variables or fields (such
231 as concentrations, density or porosity) which are also defined over portions of the same
232 domain. The domain is discretized and fields are defined over the discretized space (nodes or
233 cells). Using discretization techniques (such as finite element or finite differences methods)
234 PDEs are converted into a set of algebraic equations which represent a discrete version of the

235 PDE. For each discretized time interval, this set of equations can simultaneously be solved with
236 the AE or using an operator splitting technique.

237 The above description points to a natural class structure for our problems. The PDEs share
238 attributes such as terms in the equation, state variables or domain definitions, and also share
239 functionalities such as computing the balance or the matrices for the discretized PDE.
240 Therefore, we find it natural to define a class, termed *Phenomenon*, to identify PDEs. In the
241 same fashion, we define *Process* as the class whose instances will be specific terms in the PDE
242 (e.g. advection, dispersion, etc.). The class *Meshfields* defines objects representing various
243 properties defined over space (and time). To deal the geochemical processes we use the class
244 *CHEPROO* (CHEmical PRocesses Object Oriented, Bea et al. 2009). All these objects produce the
245 terms for the (non-linear) discretized PDEs, which are solved with the functions of the class
246 *Solver*. The class organization described above is shown in Figure 1 and its detailed description
247 is given below.

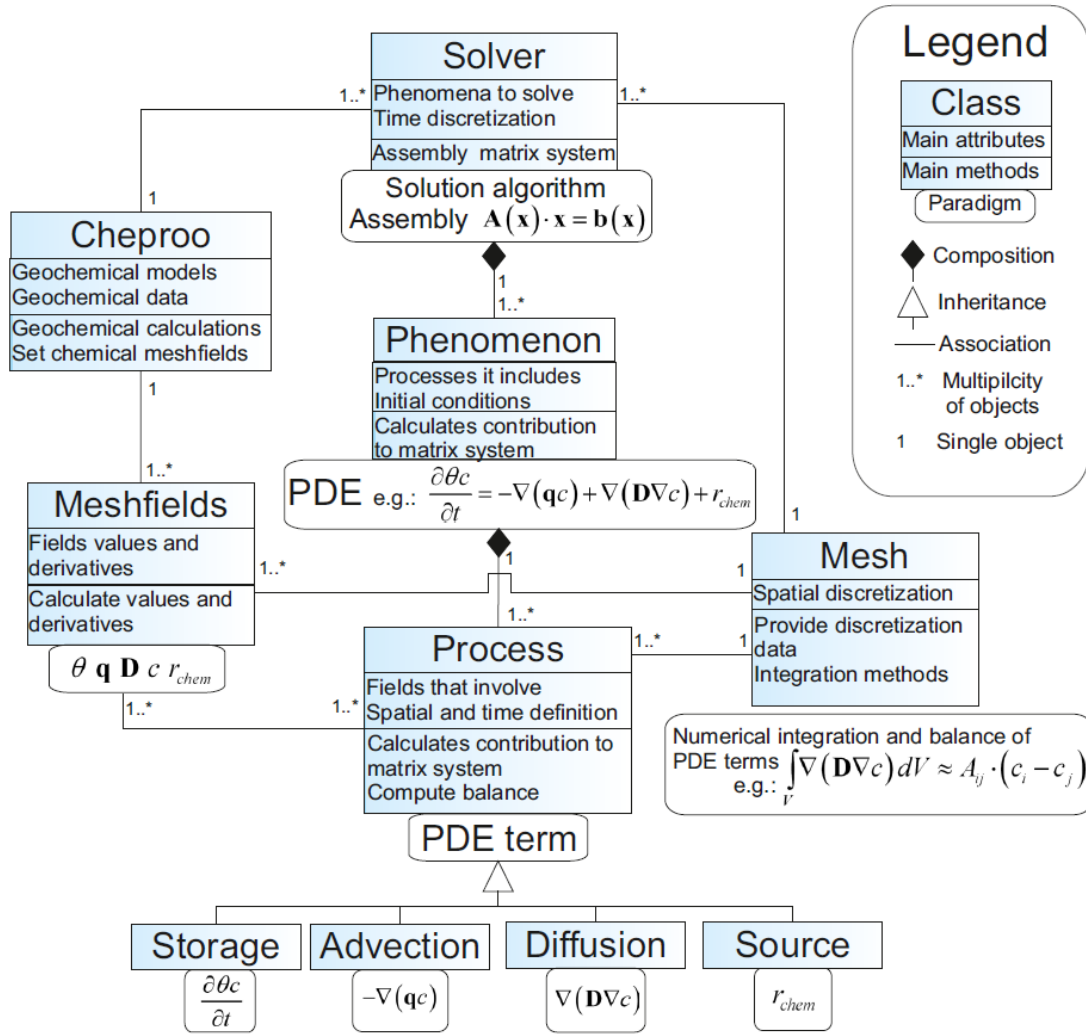


Figure 1 – Organization of main classes in PROOST. Each box represents a class with its attributes and methods. A paradigm is show below each class.

248 3.1. Phenomenon class

249 PDEs are a central ingredient of reactive transport modeling. All PDEs represent a conservation
 250 principle. All of them consist of different terms, like storage, flux divergence or source terms
 251 and are subject to initial and boundary conditions. Therefore, we define a class for
 252 representing PDEs. We term this class *Phenomenon*. Note that a number of authors have also
 253 defined similar classes in their analysis (Boivin and Ollivier-Gooch 2004, Kolditz and Bauer 2004,
 254 Meysman et al. 2003). But the main difference here is that in our case, the Phenomenon
 255 object is composed by several objects of the class Process which represent the different terms

256 of the PDE. This is a key aspect that facilitates code reuse, as will be shown below in the
257 *Process* class description.

258 Beside the *Processes* that define the PDE, the initial and boundary conditions are also the main
259 attributes of the *Phenomenon* class. Methods include the computations of balances or the
260 contribution to matrices comprising the discrete version of the PDEs. The values of the solution
261 variables or unknowns will be obtained from the solution of this matrix system.

262 Initial conditions and Dirichlet boundary conditions are defined as a *Meshfields* and are
263 handled by the *Phenomenon* Class. The rest of boundary conditions, as can be expressed as
264 different terms of the PDE, are represented by instances of the *Process* class. The Dirichlet
265 boundary conditions has the particularity of imposing the state variable value over different
266 parts of the domain. For this reason there are handled directly by the *Phenomenon*.

267 A *Phenomenon* object can be used to represent a single conservation principle (such as species
268 mass or energy) or several conservation principles with similar equations, like components
269 concentrations. For this latter case, the *Phenomenon* class makes use of the fact that the same
270 conservation equation applies to all components, and therefore only one PDE has to be
271 defined which applies to all components.

272

273 3.2. *Process* class

274 The terms that compose the PDE (e.g., storage or advection) and the boundary conditions that
275 constrain it (e.g. leakage) are represented by the *Process* class. The actual nature of this term is
276 defined via inheritance by specialization classes (Figure 1).

277 The main attributes of this class are the time and space where the *Process* is applied (for
278 example the location of a pumping well for a sink-source *Process*) and the fields it involves (the
279 pumping rate in this example). Methods include the computation of the process contribution
280 to the system matrix or to the global balance. All these are performed by using methods of the
281 class *Mesh*, where all discretization-integration information and methods are encapsulated.

282 The *Processes* objects are the terms that constitute the conservation equations. A
283 *Phenomenon* can be formulated by combining different *Processes*. This class facilitates the
284 extensibility of the code because only the new terms (new specialization of the class *Process*)
285 have to be programmed to extend the set of equations that can be solved. It also allows
286 reusing code, since the same type of *Processes* can be used for different conservation
287 equations. For example, a diffusive process for a mass conservation equation and an energy
288 conservation equation are a different instance of the same class. Another example is the
289 extension of the component conservation equation from single phase to multiphase (equation
290 (7)). For this case, all processes have to be replicate for each mobile phase. This can be easily
291 done by considering new instances of the same *Process* objects.

292 There are certain limitations regarding the kind of *Processes* that can be added to a
293 *Phenomenon*, and are related to the numerical method chosen for solving it. The nature of the
294 considered *Process* has to be supported by the numerical method. For example, in its current
295 implementation, advective terms cannot be considered when solving a PDE with the Mixed
296 Finite Element Method.

297 Most boundary conditions are represented with objects of the class *Process*. Imposed fluxes
298 and variable dependent fluxes are considered through a *Sink-Source* objects, which are
299 specialization of the class *Process*. As mentioned before Dirichlet boundary conditions are
300 handled by the *Phenomenon* class.

301

302 3.3. *Mesh class*

303 There are different techniques to solve PDEs numerically. All these techniques share an
304 approach for discretizing the spatial domain (such as nodes, elements or cells) and methods to
305 integrate (or differentiate) the terms (*Process*) of a PDE (*Phenomenon*) to produce a matrix
306 system from which the discrete solution of the PDE can be obtained.

307 Thus, all the data and functionality regarding spatial discretization and the discretization-
308 integration methods for solving PDE (such as finite element or finite differences) define a class
309 that we term *Mesh*. A number of authors have defined similar classes in their analysis.
310 However, most of them separate the domain discretization from the integration methods in
311 different classes (Commend and Zimmermann 2001, Wang and Kolditz 2007). This integration
312 was made because, despite of the fact that both methods can share a mesh (elements and
313 nodes), the mesh topological data required might be different. For example, Mixed Finite
314 Elements and Finite Elements can both use the same mesh, but Mixed Finite Elements needs
315 extra information about edges for 2D problems or sides for 3D. Another difference between
316 these two methods is that while Finite Elements gives a continuum scalar field for the solution
317 over the mesh, Mixed Finite Elements gives a vector field. Therefore, some aspects of the
318 spatial discretization are related to the integration method, and that is why both are consider
319 in a single object in PROOST.

320 The main attributes of the *Mesh* class are the domain discretization information (such as nodes
321 or cell coordinates and connectivity between these discrete elements). Methods include
322 yielding information of space discretization (such as the number of discrete elements and their
323 geometrical information), integrating the different terms of the conservation equation
324 (*Processes*) over the domain, and evaluating spatial properties of variables such as gradients.

325 The *Mesh* class allows incorporating new discretization-integration numerical methods by
326 adding new specializations of the class. Two specializations of the class *Mesh* are currently
327 implemented in PROOST: the Finite Elements and the Mixed Finite Elements.

328

329 *3.4. Meshfield class*

330 Another important element of reactive transport modeling is the AEs that represent
331 constitutive and thermodynamic laws. Constitutive laws express one field as a function of
332 others. Thus a class termed *Meshfield* is defined to represent the projection of different scalar,

333 vector or tensor fields (such as pressure, flux or conductivity) in the discrete domain. The main
334 attributes of this class are the values and derivatives of a field for the discrete entities (nodes,
335 elements or cells) and the parameters of the function or constitutive laws they represent. The
336 main methods of the class are to calculate its values and derivatives, and to interpolate its
337 values over any point of the domain. Among others, *Meshfield* is used to represent retention
338 curves, relative permeability curves and dispersion coefficients.

339 For example a flux *Meshfield* object defined as $\mathbf{q} = -\mathbf{T}\nabla h$, can calculate its values and its
340 derivatives to transmissivity \mathbf{T} and head h fields. When a *Meshfield* represents one of the
341 solution variables of the problems, like head in the previous example, its values are set by the
342 solver class.

343 The *Meshfield* class facilitates code extension since new constitutive laws can be easily added
344 to the code by creating new specializations.

345

346 3.5. *CHEPROO* class

347 Geochemical calculations for the component concentrations and kinetic rate laws of equation
348 (4) are in fact constitutive laws. Hence, we treat them as a specialization of a *Meshfield*, which
349 we term *Chemical Meshfield*. Many geochemical variables affect the evolution of the system
350 but do not appear explicitly in any PDE (e.g. the activity of aqueous species). For this reason
351 and also because of the complexity of some geochemical calculations, all geochemical models
352 and computations are encapsulated into a single object of a class termed *CHEPROO*. Only the
353 chemical variables that appear in PDE (such as component concentration or density) are stored
354 in a *Chemical Meshfield*.

355 The *CHEPROO* class uses a module with the same name, with an internal class hierarchy
356 including classes like species, phase and reaction (Bea et al.2009). *CHEPROO* attributes include
357 the geochemical models, such as those for activity coefficients, density or kinetic rates laws,
358 and the chemical data associated to each discrete point of the problem, such as concentrations

359 or components definition. *CHEPROO* includes methods for calculating the values and
360 derivatives of chemical variables (like component concentration) with respect to the solution
361 variables of the PDE, and to dump them into *Chemical Meshfield* objects.

362 *CHEPROO* also controls the number of chemical components. For some formulations, like the
363 one of Saaltink et al. (1998), the number of components may change in time and space. Thus,
364 *CHEPROO* has to provide information about the components in order to establish the
365 dimension of the final matrix system to be solved.

366 3.6. *Solver* class

367 A coupling strategy (coupled or decoupled) needs to be chosen when solving several PDEs. A
368 solution technique for non-linear systems (Newton-Raphson or Picard) is also needed. An
369 object of the *Solver* class will be in charge of solving a number of PDEs with a chosen solution
370 strategy:

- 371 • Independently, there are no crossed influences between *Phenomena* (for example changes
372 on porosity due to chemical changes are not considered when solving fluid phase
373 conservation)
- 374 • Sequentially, influences between *Phenomena* are considered lagged in time (for the
375 porosity example, changes due to chemistry in time t are considered for flow in time $t + dt$)
- 376 • Iteratively, all *Phenomena* are alternately solved until no significant changes on linking
377 variables occurs (for the porosity example, flow and transport are solved alternately until
378 no significant changes in porosity occurs)

379 Coupled, all *Phenomena* are solved at once. *Solver* attributes include the set of *Phenomena*,
380 the coupling strategy, the time discretization parameters or the convergence criteria. Methods
381 are required for assembling and solving the discretized PDE system, for time integration. To
382 address these, *Solver* uses other classes. For instances, matrix systems are handled by a class
383 termed *Matrix* that encapsulates matrix data and solution techniques for linear systems.

384 *Solver* is the class that contributes most to the flexibility of the code since it can be used to
 385 solve several conservation equations following different strategies. For example, it might be
 386 used to solve first a steady state phase conservation equation (for phase flow calculation) and
 387 then a transient component conservation. Or it can be used to solve simultaneously the
 388 component and energy conservation.

389

390 3.7. Component conservation Phenomenon for the SIA and DSA approach

391 Despite the fact that the SIA and DSA are two approaches for solving the same *Phenomenon*,
 392 (the component conservation equation), the way this *Phenomenon* is formulated in PROOST
 393 depends on the chosen approach.

394 When solving component conservation equations with the DSA approach the input
 395 Phenomenon for PROOST should be the same as in equation (7). However, for the SIA
 396 approach immobile species storage and kinetic reactions are treated as a sink-source term :

$$397 \quad f_{SIA_i} = -\sum_{\beta} \frac{\partial}{\partial t} (\theta_{\beta} u_{i,\beta}) + k_{u_i} \quad (8)$$

398 Thus the component conservation equation is written only in terms of mobile component
 399 conservation:

$$400 \quad \sum_{\alpha} \frac{\partial}{\partial t} (\theta_{\alpha} u_{i,\alpha}) = \sum_{\alpha} L_{\alpha} (u_{i,\alpha}) + f_{SIA_i} + f_{u_i} \quad (9)$$

401 The Proost class organization allowed implementing the SIA method without many
 402 modifications. The SIA sink source term was represented with the preexisting sink-source
 403 *Process* class. This process evaluates the values of the sink source term, which are given by a
 404 *Meshifield*, and calculates its contribution to the discretized PDE system. By doing this, all the

405 complexity of this term is encapsulated in the class Cheproo, which sets the values of the SIA
406 source term in a *Chemical Meshfield*.

407

408 **4. Solution procedure scheme for a time step**

409 The interaction between PROOST objects can be illustrated by the solution of a time interval
410 for a reactive transport problem considering the DSA method. The flow diagram is shown in
411 Figure 2, from which 15 relevant points have been identified.

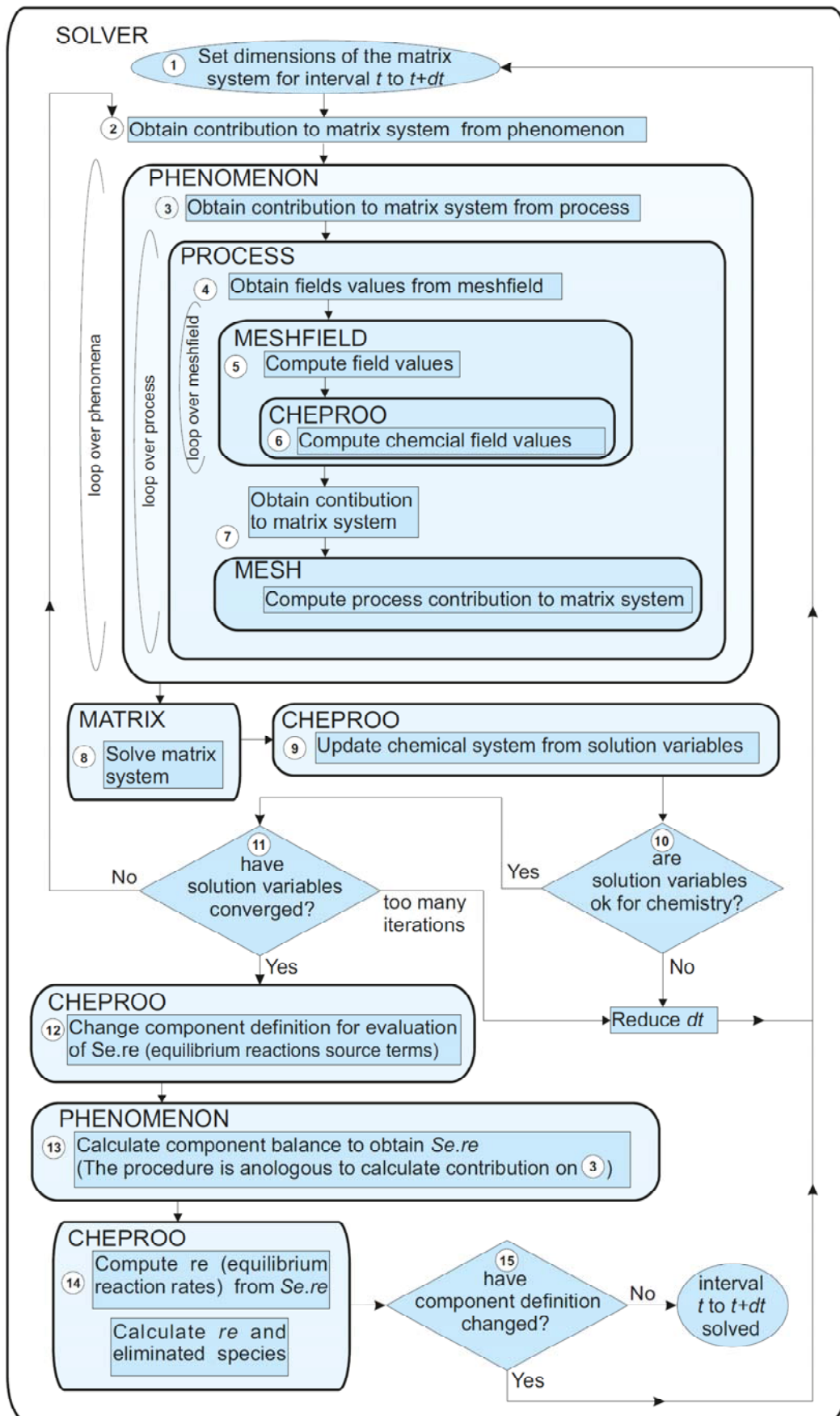


Figure 2 – Flow diagram of a time interval resolution for a reactive transport problem in PROOST

- 412 1. *Solver* establishes the size of the matrix system to be solved. This size depends on the
413 number of coupled phenomena and the dimension of each state variable. Recall that
414 component conservation dimension can be different for each discrete point and may
415 change among the iterative process.
- 416 2. *Solver* assembles the matrix system to be solved. To this end, *Solver* requests each
417 *Phenomenon* for its contribution.
- 418 3. *Phenomenon* requests for the contribution of all its *Processes*.
- 419 4. Each *Processes* request the values of all the *Meshfields* to which it is related.
- 420 5. *Meshfield* computes its values.
- 421 6. *CHEPROO* calculates *Chemical Meshfield* values.
- 422 7. *Mesh* computes the contribution of the *Process* to the matrix system.
- 423 8. *Matrix* solves the matrix system.
- 424 9. *Solver* updates the calculated solution variables (concentrations, temperature or
425 pressures) in *CHEPROO*.
- 426 10. *CHEPROO* calculates the concentration of all species from these values (speciation). If
427 there are significant changes on chemical composition, like complete dissolution of
428 minerals in equilibrium or precipitation of new ones, geochemical calculation might not
429 converge. If that is the case, the length of time interval is reduced and the resolution
430 procedure is restarted. The user sets the ideal time step, but if the resolution of the matrix
431 system (which goes from step 2 to 11) exceeds a certain number of iterations, also set by
432 the user, the time step is reduced.
- 433 11. *Solver* controls the convergence of the PDEs linearization and resolution process. When
434 convergence is reached all variables involved in the *phenomena* are known, except
435 equilibrium reactions rates that were eliminated when solving component conservation
436 (equation (7)). These rates can be calculated from the species conservation equations
437 (equation (2)). In order to avoid the formality of formulating both components and species

438 *Phenomenon*, this is done by considering an alternative component definition; each mobile
439 species is considered a component. Therefore, the result of the balance of the new
440 component conservation will be the product of the stoichiometric coefficient and the
441 equilibrium reaction rates. These aspects are illustrated with an example in the next
442 section.

443 12. *CHEPROO* changes component definition (each mobile species is considered a component).
444 This step allows solving species conservation equations with the same structure used for
445 component conservation equations. This is one of the advantages of Proost class
446 organization. More details on this particular aspect will be given in section 6.

447 13. *Phenomenon* computes balance (similar to step 3).

448 14. *CHEPROO* calculates equilibrium reaction rates from *Phenomenon* balance. Some reactive
449 transport formulations, like the one of Saaltink et al. (1998), eliminate constant activity
450 species, like minerals, from component composition. These species concentration can be
451 calculated once the equilibrium reaction rates are known.

452 15. If the formulation considered eliminates constant activity species, the number of
453 component is affected by the disappearance or appearance of minerals. Therefore,
454 component definition has to be controlled after the eliminated species were calculated. If
455 component definition changes the resolution procedure has to be started for the new
456 definition, if not the resolution procedure for the time step is finished.

457

458 5. Code implementation

459 The code presented results from merging and expanding two existing codes: PROOST and
460 CHEPROO. The original design of PROOST was already capable of solving different
461 phenomena, in a coupled or decoupled way, by considering different techniques for the
462 resolution of non-linear system (such as Newton-Raphson or Picard). However, such a design
463 only allowed solving *Phenomenon* objects that had one scalar field as unknown. Also

464 Phenomenon Processes had to be written explicitly as a function of the unknown variable.
465 These featured clashed with the resolution of component conservation, especially when the
466 DSA approach is considered.

467 The solution of component conservation equations involves considering the conservation
468 equation of several components. As the number of components and its definition might
469 change in time and space (because of complete dissolution or appearance of new mineral
470 species), the number of *Phenomenon* considered would also have to vary. In order to avoid
471 this difficulty, and as the same *Processes* affect all component concentrations, only one
472 *Phenomenon* is considered which applies to a vector variable: the component concentration
473 vector. Therefore, *Phenomenon* and *Process* classes were expanded to handle a vector variable
474 whose size may change in time and space.

475 Processes were originally designed to represent terms of PDEs that directly involve the
476 unknowns of the problem (i.e. main state variables of the phenomenon: pressure for flow
477 equation, concentration for transport equation). For example, all *Processes* in a conservative
478 transport problem involve the solute concentration variable, which is also the unknown of this
479 problem. When solving reactive transport by the DSA method *Processes* are formulated in
480 terms of component concentrations, but the unknowns of the problem are the primary species
481 concentrations. Therefore, *Phenomenon* and *Process* classes were expanded so they can be
482 formulated in terms of any variable and not necessarily the unknown.

483 Originally, CHEPROO was capable of solving single phase reactive transport problems.
484 CHEPROO uses a matrix system calculated by another conservative transport code to
485 formulate and solve the reactive transport problem (Bea et al. 2008). In order to take
486 advantage of PROOST's flexibility we choose to formulate and solve the multiphase reactive
487 transport equations in PROOST instead of CHEPROO. Therefore, CHEPROO was added to the
488 PROOST structure with the only purpose of performing the chemical calculations (speciation)
489 and provide geochemical variables values and derivatives.

490 Besides adding new services to make chemical variables available outside its module, several
491 improvements were made in CHEPROO. Phase properties like density, viscosity and enthalpy,
492 and capillary effect on water activity were added. The PROOST class organization allowed
493 representing all this chemical variables in the class *Chemical meshfield*. By doing this all the
494 work related to the evaluation, update and dependency of these fields to others (like pressure
495 or temperature) is done by pre existing methods.

496 Also a new speciation algorithm that uses the Newton-Raphson method had to be
497 programmed in CHEPROO due to the high nonlinearity of concentrated solutions. CHEPROO
498 and PROOST were programmed in FORTRAN 95 following the OO paradigm. This language was
499 chosen for its high popularity among hydrogeologists and its excellent performance reputation.
500 Even though FORTRAN is not a full object-oriented language it can directly support many of the
501 important concepts of OO programming. Details about OOP concepts in FORTRAN can be
502 found in Akin (1999), Carr (1999), Decyk et al. (1998), Gorelik (2004), Maley et al. (1996) and
503 Norton et al. (1998).

504

505 **6. Application:**

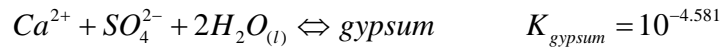
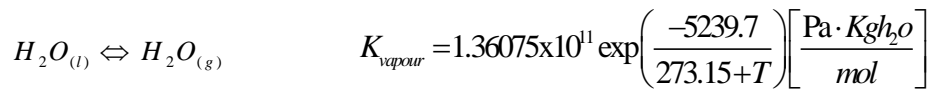
506 6.1. Application Description

507 In order to illustrate the classes introduced before, some aspects of the solution procedure
508 scheme for a time step (generically described in section 4) are shown for a concrete
509 application. We present the modeling of a 24 cm column of porous gypsum subjected to a
510 constant source of heat, in which a significant evaporation occurs. We will focus on the
511 component conservation equation. This synthetic example was designed for illustrating the
512 interaction between hydrodynamic and geochemical processes and it is described in detail by
513 Gamazo et al. (2012). Due to this interaction a compositional formulation was adopted and
514 therefore no phase conservation equations are explicitly solved. The finite element method
515 was used for the spatial discretization. One of the most interesting aspect of the application is
516 how the equilibrium reaction rates were calculated. This implies solving a different
517 conservation equation, species conservation instead of components. The PROOST structure
518 allowed to calculate the equilibrium reaction rates by using preexisting methods.

519 This application example includes gypsum, liquid water and vapor, dissolved and gaseous air,
 520 calcium and sulfate (main components of gypsum besides water) and 2 conservative species
 521 potassium and chloride (see Table 2). It also considers the occurrence of anhydrite, which may
 522 precipitate as a result of gypsum dehydration. Note that the coexistence in equilibrium of
 523 anhydrite and gypsum can fix water activity and therefore produce invariant points (Risacher
 524 and Clement 2001). As was exposed above, to our knowledge, PROOST is the first multiphase
 525 reactive transport capable of modeling this scenario.

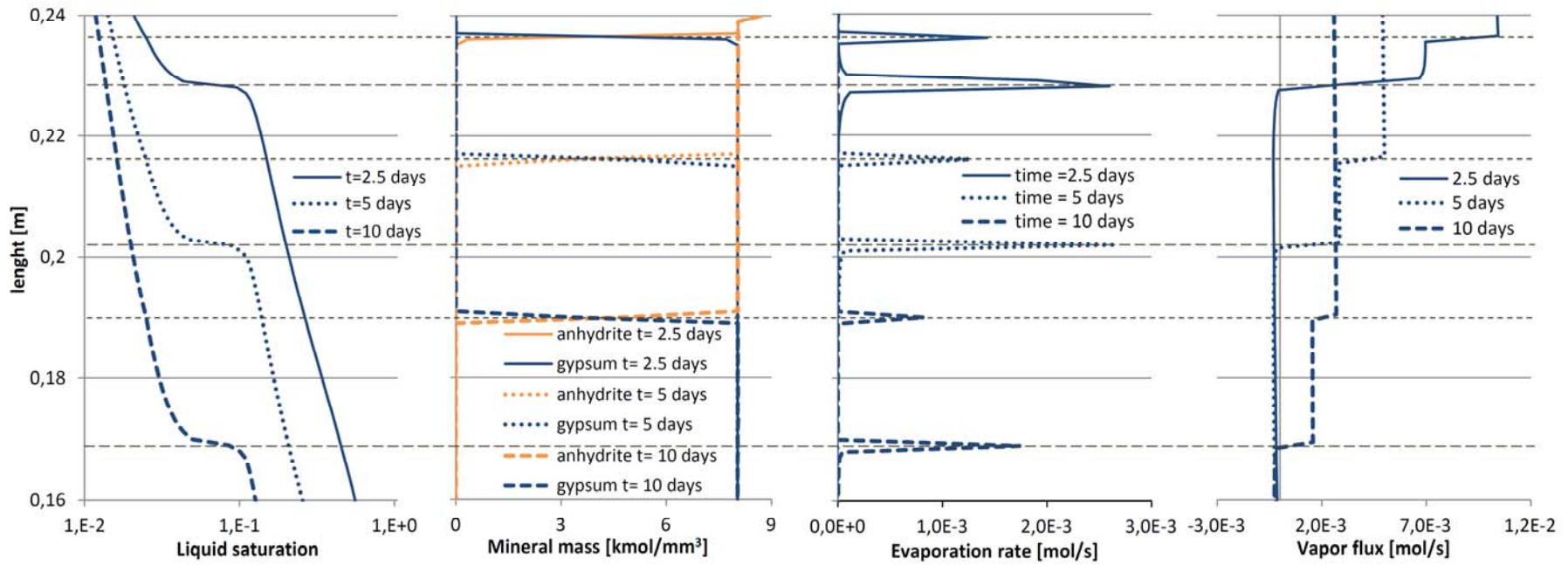
526 Table 2 – Chemical species and reactions considered

$h_2o_{(l)}, h_2o_{(g)}, air_{(l)}, air_{(g)}, Ca, So_4, K, Cl, gypsum, anhydrite$



527 6.2. Initial component definition

528 Pore solution was initially considered in equilibrium with gypsum with a mineral volumetric
 529 content of 0.6. The incoming energy heats the column, which increases evaporation and
 530 reduces saturation degree at the top. This induces an ascending non saturated flow of liquid
 531 water. At certain point a descending evaporation front appears followed by an also descending
 532 gypsum dehydration front in which anhydrite precipitates (see Figure 3). Note that this second
 533 front has a significant effect on vapor flow.



534

535

Figure 3 – Liquid saturation, mineral mass, evaporation rate and vapor flux for the upper 8 cm of the column. Note that besides the typical evaporation front associated to the drying front

536

there is a second evaporation front associated to hydrated mineral dissolution. This second front has a significant effect on vapor flow.

537 When the simulation starts the whole domain has the same mineral composition and
 538 therefore the component conservation equations for all nodes are the same (see Table 3 for
 539 component definition):

$$540 \quad \frac{\partial}{\partial t} \theta_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h_2o} - 2c_{SO_4^{2-}} \end{pmatrix} + \frac{\partial}{\partial t} \theta_g \begin{pmatrix} 0 \\ c_{air(g)} \\ 0 \\ 0 \\ c_{h_2o(g)} \end{pmatrix} = -\nabla \cdot \left(\mathbf{q}_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h_2o} - 2c_{SO_4^{2-}} \end{pmatrix} \right) + \nabla \cdot \left(\mathbf{D}_{aq} \nabla \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h_2o} - 2c_{SO_4^{2-}} \end{pmatrix} \right) - \nabla \cdot \left(\mathbf{q}_g \begin{pmatrix} 0 \\ c_{air(g)} \\ 0 \\ 0 \\ c_{h_2o(g)} \end{pmatrix} \right) + \nabla \cdot \left(\mathbf{D}_g \cdot \nabla \begin{pmatrix} 0 \\ c_{air(g)} \\ 0 \\ 0 \\ c_{h_2o(g)} \end{pmatrix} \right) + \begin{pmatrix} 0 \\ f_{air(g)} \\ 0 \\ 0 \\ f_{h_2o(g)} \end{pmatrix} \quad (10)$$

541 This implies that the number of components is the same for the entire domain. This aspect is
 542 controlled by a single object of the *Cheproo* class, and affects almost all classes: from the
 543 *Solver*, in charge of calculating the dimension of the system to be solved, to the *Meshfiled*, in
 544 charge of storing field values and their derivatives to state variables.

545 Table 3 – Component definition for different mineral combinations (from up to down: only gypsum, gypsum and
 546 anhydrite, only anhydrite) and the “one component per mobile species” component definition \mathbf{U}_1 .

$$\mathbf{U}_{gypsum} = \begin{bmatrix} & H_2O_{(l)} & air_{(l)} & Ca^{2+} & SO_4^{2-} & K^+ & Cl^- & H_2O_{(g)} & air_{(g)} & anh & gyp \\ u_K & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ u_{air} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ u_{Ca-SO_4} & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_{Cl} & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ u_{h_2o-2SO_4} & 1 & 0 & 0 & -2 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_{anh-gyp} = \begin{bmatrix} & H_2O_{(l)} & air_{(l)} & Ca^{2+} & SO_4^{2-} & K^+ & Cl^- & H_2O_{(g)} & air_{(g)} & anh & gyp \\ u_K & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ u_{air} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ u_{Ca-SO_4} & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_{Cl} & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_{anhydrite} = \begin{bmatrix} & H_2O_{(l)} & air_{(l)} & Ca^{2+} & SO_4^{2-} & K^+ & Cl^- & H_2O_{(g)} & air_{(g)} & anh & gyp \\ u_K & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ u_{air} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ u_{Ca-SO_4} & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_{Cl} & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ u_{h_2o} & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_1 = \begin{bmatrix} & H_2O_{(l)} & air_{(l)} & Ca^{2+} & SO_4^{2-} & K^+ & Cl^- & H_2O_{(g)} & air_{(g)} & anh & gyp \\ u_{h_2o(l)} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_{air(l)} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_{Ca} & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_{SO_4} & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ u_K & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ u_{Cl} & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ u_{h_2o(g)} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ u_{air(g)} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

547 Despite of having several components, each with its own conservation equation or
548 phenomenon, PROOST treats components as entities pertaining to one phenomenon. This
549 simplifies the code's internal operability and problem definition, since it allows taking benefit
550 of the fact that several processes affect species in the same way. For example the storage,
551 advection and diffusion-dispersion processes in equation (10) affect all species from a phase in
552 the same way. For these processes the contribution to the system matrix are calculated for all
553 components together. Encapsulation allows confining to the *Process* class all the complexity
554 associated to the fact that processes can be part of one or a set of partial differential equations.
555 Currently the only process that acts differently over each species is the "sink/source" process.

556 The Cheproo object also defines which species and variables will be considered as state
557 variables for Newton-Raphson system. When only gypsum is present in the system, the states
558 variables associated to component conservation equations are: c_{K^+} $c_{air(l)}$ $c_{Ca^{2+}}$ c_{Cl^-} P_1 . The rest
559 of species ($c_{air(g)}$, $c_{h_2o(g)}$, $c_{SO_4^{2-}}$) are secondary and its values are calculated by Cheproo by

560 considering mass actions laws. Reaction rates and non-mobile species concentrations are
561 calculated in a subsequent step.

562 In order to understand the physical meaning of component conservation equations, it is
563 helpful to associate state variables to specific components. For example, each of the species
564 chosen as state variables (c_{K^+} , $c_{air(l)}$, $c_{Ca^{2+}}$ and c_{Cl^-}) can be considered as the constituents of
565 the four first components of the conservation equations (10). The association of the liquid
566 pressure (p_l) to a specific component is not straight forward. Liquid pressure is related to
567 liquid saturation which affects all components. Since the last component in equation (10)
568 contains all water species and only involves secondary species, liquid pressure can then be
569 associated to its main variable. However, variables like activity coefficients, density, viscosity,
570 gas pressure and liquid saturation, depend on all state variables and make the system fully
571 coupled. Nevertheless, the exercise of defining a main variable for every component provides
572 a more profound knowledge about variables dependency, which may be relevant for some
573 cases as will be shown in section 6.3. For that case water species is eliminated from the
574 component equation and both calcium and sulfate are defined as secondary variables.

575 As can be seen in Figure 2, matrix system assembling is the core of a time interval resolution. It
576 involves all the classes shown in Figure 1.

577 Once the system is solved there are still unknown variables to be calculated: the eliminated
578 species concentration and the equilibrium reaction rates.

579 These variables can be calculated by considering the species conservation equation. In order to
580 avoid formulating a different phenomenon the PROOST class organization allows using the
581 same structure as used for calculating component conservation for species conservation. This
582 is one of the advantages of the Proost class organization. The same phenomenon is considered

583 and only the component definition is changed. The new component definition considers every
 584 mobile species as a component (see Table 3):

$$\begin{aligned}
 585 \quad & \frac{\partial}{\partial t} \theta_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(i)} \\ 0 \\ c_{Ca^{2+}} \\ c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(i)} \\ 0 \end{pmatrix} + \frac{\partial}{\partial t} \theta_g \begin{pmatrix} 0 \\ 0 \\ c_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} = -\nabla \cdot \mathbf{q}_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(i)} \\ 0 \\ c_{Ca^{2+}} \\ c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(i)} \\ 0 \end{pmatrix} + \nabla \cdot \mathbf{D}_{aq} \cdot \nabla \begin{pmatrix} c_{K^+} \\ c_{air(i)} \\ 0 \\ c_{Ca^{2+}} \\ c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(i)} \\ 0 \end{pmatrix} \\
 & - \nabla \cdot \mathbf{q}_g \begin{pmatrix} 0 \\ 0 \\ c_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} + \nabla \cdot \mathbf{D}_g \cdot \nabla \begin{pmatrix} 0 \\ 0 \\ c_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ f_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ f_{h2o(g)} \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ -1 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \\ 0 & -1 & -2 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} r_{air} \\ r_{h2o} \\ r_{gyp} \end{pmatrix} \quad (11)
 \end{aligned}$$

586 Note that all the processes in equation (11) are analogous to equation (10), except the last one.
 587 This is the only term in equation (11) that has unknown variables (r_{air} , r_{h2o} , r_{gypsum}), the other
 588 terms involve known variables. In order to calculate these unknown variables the \mathbf{U}_1
 589 component definition is considered and a general method of the *process* class, balance, is used
 590 to calculate all terms at the right hand side of equation (9):

$$\begin{aligned}
 591 \quad & \begin{pmatrix} 0 \\ -r_{air} \\ r_{air} \\ -r_{gyp} \\ -r_{gyp} \\ 0 \\ -r_{h2o} - 2r_{gyp} \\ r_{h2o} \end{pmatrix} = \frac{\partial}{\partial t} \theta_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(i)} \\ 0 \\ c_{Ca^{2+}} \\ c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(i)} \\ 0 \end{pmatrix} + \frac{\partial}{\partial t} \theta_g \begin{pmatrix} 0 \\ 0 \\ c_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} + \nabla \cdot \mathbf{q}_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(i)} \\ 0 \\ c_{Ca^{2+}} \\ c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(i)} \\ 0 \end{pmatrix} \\
 & - \nabla \cdot \mathbf{D}_{aq} \cdot \nabla \begin{pmatrix} c_{K^+} \\ c_{air(i)} \\ 0 \\ c_{Ca^{2+}} \\ c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(i)} \\ 0 \end{pmatrix} + \nabla \cdot \mathbf{q}_g \begin{pmatrix} 0 \\ 0 \\ c_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} - \nabla \cdot \mathbf{D}_g \cdot \nabla \begin{pmatrix} 0 \\ 0 \\ c_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} - \begin{pmatrix} 0 \\ 0 \\ f_{air(g)} \\ 0 \\ 0 \\ 0 \\ 0 \\ f_{h2o(g)} \end{pmatrix} \\
 592 \quad & (12)
 \end{aligned}$$

593 The result is used by Cheproo to calculate the reaction rates (evaporation, volatilization of
 594 dissolved air and gypsum precipitation). Note that the number of equations exceeds the
 595 number of unknowns (eight and three, respectively). In theory, solution of all equations should
 596 give the same reactions rates. For simplicity we used the least square method for the solution
 597 of equation (9). Once the reaction rates are calculated, the mole variations of mineral species
 598 can be computed (gypsum for this case). If a mineral is completely depleted or if the solution
 599 has become saturated for a new mineral, components should be redefined and calculations for
 600 the time step recalculated.

601 6.3. Anhydrite precipitation

602 As the system evolves over time, water activity decreases at the top of the column due to
 603 osmotic and capillary effect, and anhydrite starts to precipitate. When anhydrite and gypsum
 604 coexists a singularity, known as “invariant point”, occurs and water activity remains constant
 605 (Risacher and Clement 2001 and Gamazo et al. 2011). Combining the mass actions law for
 606 anhydrite and gypsum (equation (13)) the fixed water activity value can be obtained:

$$607 \quad a_{Ca^{2+}} a_{SO_4^{2-}} = K_{anhydrite} \Rightarrow a_{h2O(l)} = \sqrt{\frac{K_{gypsum}}{K_{anhydrite}}} \quad (13)$$

$$a_{Ca^{2+}} a_{SO_4^{2-}} a_{h2O(l)}^2 = K_{gypsum}$$

608 Under this scenario gypsum dissolves and anhydrite precipitates at a rate that ensures this
 609 fixed water activity:



611 This implies a singular component definition (see Table 3) which results in the following
 612 component conservation equation:

$$613 \quad \frac{\partial}{\partial t} \theta_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \end{pmatrix} + \frac{\partial}{\partial t} \theta_g \begin{pmatrix} 0 \\ c_{air(s)} \\ 0 \\ 0 \end{pmatrix} = -\nabla \cdot \left(\mathbf{q}_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \end{pmatrix} \right) + \nabla \cdot \left(\mathbf{D}_{aq} \cdot \nabla \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \end{pmatrix} \right) - \nabla \cdot \left(\mathbf{q}_g \begin{pmatrix} 0 \\ c_{air(s)} \\ 0 \\ 0 \end{pmatrix} \right) + \nabla \cdot \left(\mathbf{D}_g \cdot \nabla \begin{pmatrix} 0 \\ c_{air(s)} \\ 0 \\ 0 \end{pmatrix} \right) + \begin{pmatrix} 0 \\ f_{air(s)} \\ 0 \\ 0 \end{pmatrix} \quad (15)$$

614 Note that all forms of water have been eliminated from the components conservation
 615 equation. For all nodes where anhydrite and gypsum coexists these new components have to
 616 be considered, and the states variables associated to conservation equation will be: c_{K^+} , $c_{air(l)}$,

$$617 \quad c_{Cl^-}, P_l.$$

618 This conservation equation, and the corresponding states variables, may make it difficult to
 619 associate state variables to specific components. As in the previous system, the state variables
 620 c_{K^+} , $c_{air(l)}$, c_{Cl^-} can be associated to the first, second and fourth component respectively.

621 Hence, the remaining variable, liquid pressure, must be associated to the third component of
 622 equation (15). Although this third component only contains Ca^{2+} and SO_4^{2-} and no H_2O , it still

623 depends on liquid pressure through volumetric content, θ_{aq} , and retention curve. Hence, there
624 is no problem in using it for the calculation of liquid pressure. But since neither $c_{Ca^{2+}}$ or
625 $c_{SO_4^{2-}}$ are state variables, it is not straight forward to understand how the system can manage
626 balance of these two species, especially when advective and diffusive fluxes are considered. In
627 nodes where gypsum and anhydrite coexists water activity is fixed. The main mechanism for
628 this is the sink source term of water produced by the interaction of these two minerals as
629 shown in equation (14). But this interaction can also affect calcium and sulfate concentration
630 through differences in precipitation rates. For instance, if the rate of gypsum dissolution is the
631 same as anhydrite precipitation then only water is released. But any differences between
632 these rates can release or consume dissolved Ca^{2+} and SO_4^{2-} . Hence, gypsum-anhydrite
633 interaction will release the necessary amount of water, calcium and sulfate to keep water
634 activity constant and to conform these two species conservation equations. This can be seen
635 by considering the species conservation equation of calcium and sulfate ((16) and (17)), and
636 the sum of liquid and gaseous water (18):

637

$$638 \quad \frac{\partial}{\partial t} \theta_{aq} (c_{Ca^{2+}}) = -\nabla \cdot (\mathbf{q}_{aq} (c_{Ca^{2+}})) + \nabla \cdot (\mathbf{D}_{aq} \cdot \nabla (c_{Ca^{2+}})) - r_{gyp} - r_{anhy} \quad (16)$$

$$639 \quad \frac{\partial}{\partial t} \theta_{aq} (c_{SO_4^{2-}}) = -\nabla \cdot (\mathbf{q}_{aq} (c_{SO_4^{2-}})) + \nabla \cdot (\mathbf{D}_{aq} \cdot \nabla (c_{SO_4^{2-}})) - r_{gyp} - r_{anhy} \quad (17)$$

$$640 \quad \frac{\partial}{\partial t} \theta_{aq} (c_{h2o(l)}) + \frac{\partial}{\partial t} \theta_g (c_{h2o(g)}) = -\nabla \cdot (\mathbf{q}_{aq} (c_{h2o(l)})) + \nabla \cdot (\mathbf{D}_{aq} \cdot \nabla (c_{h2o(l)})) - \nabla \cdot (\mathbf{q}_g c_{h2o(g)}) + \nabla \cdot (\mathbf{D}_g \cdot \nabla (c_{h2o(g)})) + f_{h2o(g)} - 2 \cdot r_{gyp} \quad (18)$$

641

642 The most interesting aspect of this is that the precipitation dissolution rates were eliminated
643 and therefore were not involved in the component conservation equations. This situation
644 continues as long as the two minerals coexist. If that is not the case, and one mineral is
645 depleted, the component definition is changed and the time step is recalculated.

646

647 When a mineral content is exhausted during the resolution of a time step , the new
648 component definition considers that this mineral is no longer present. However it was still
649 present at the beginning of the time step. In order to keep track of this remaining amount of
650 mineral, this amount is distributed among the species that forms it and treated as a fixed
651 source term. In the present application, when gypsum disappears, a new component definition
652 is considered ($\mathbf{U}_{anhydrite}$) and a source term is added for calcium, sulfate and water equal to the
653 amount of remaining gypsum times the corresponding stoichiometric constant, 1 for calcium
654 and sulfate and 2 for liquid water.
655 The resulting component conservation equations are similar to the ones shown in equation
656 (10).

657

$$658 \quad \frac{\partial}{\partial t} \theta_{aq} \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(l)} \end{pmatrix} + \frac{\partial}{\partial t} \theta_g \begin{pmatrix} 0 \\ c_{air(g)} \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} = -\nabla \cdot \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(l)} \end{pmatrix} + \nabla \cdot \begin{pmatrix} c_{K^+} \\ c_{air(l)} \\ c_{Ca^{2+}} - c_{SO_4^{2-}} \\ c_{Cl^-} \\ c_{h2o(l)} \end{pmatrix} - \nabla \cdot \begin{pmatrix} 0 \\ c_{air(g)} \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} + \nabla \cdot \begin{pmatrix} 0 \\ c_{air(g)} \\ 0 \\ 0 \\ c_{h2o(g)} \end{pmatrix} + \begin{pmatrix} 0 \\ f_{air(g)} \\ 0 \\ 0 \\ f_{h2o(g)} \end{pmatrix} \quad (19)$$

659 Note that the last component only involves liquid and gaseous water.

660

661 7. Summary and conclusions

662 An object oriented multiphase reactive transport class organization has been presented. It was
663 designed to ensure extensibility and flexibility. Its main classes are: *Mesh* (contains all the
664 discretization information and integration methods, such as finite elements or finite
665 differences), *Meshfield* (represent spatial fields and the constitutive laws that relate them, like
666 saturation or concentrations), *Phenomenon* (represents the conservation of a physical
667 magnitude expressed as a partial differential equation (PDE), such as mass or energy
668 conservation), *Process* (represents a term of a *Phenomenon* PDE, like advection or storage, and
669 non-Dirichlet boundary conditions), *Solver* (controls the coupling strategy for solving all

670 *Phenomena* and assembles the matrix system to solve) and *CHEPROO* (encapsulates all
671 thermodynamic data and perform geochemical calculations).

672 The flexibility and extensibility of PROOST come from the following particularities of its design.

673 Several *Phenomenon* can be formulated by combining the available *Process*. In order to solve a

674 new kind of *Phenomenon*, only new *Processes* have to be programmed. The *Solver* class can be

675 set to solve all *Phenomena* independently, sequentially or coupled.. New constitutive laws can

676 be easily added to the code by creating new specialization of the *Meshfield* class, and new

677 numerical methods for discretization-integration of PDE can be added by implementing new

678 specializations of the *Mesh* class. The main challenging task, for solving reactive transport

679 problems, was to implement the ability of using changing definitions of components. This

680 could be achieved by considering the components as entities pertaining to one *Phenomenon*.

681 The flexibility of the structure allowed the implementation of the SIA method by mainly

682 creating a new specialization of the *Meshfield* class. The performance of PROOST is illustrated

683 by describing the solution procedure for a concrete application: the modeling of a column of

684 porous gypsum subjected to a constant source of heat. The problem involves important

685 interaction between hydrodynamic and geochemical processes like the occurrence of invariant

686 points. The flexibility of the structure is shown in the example. In this regard, it highlights the

687 fact that a single phenomenon object is considered for representing both component and

688 species conservation in two different steps of the resolution procedure. This allows the

689 calculation of the equilibrium reaction rates using pre existing methods.

690

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