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Benchmarks for multicomponent diffusion and electrochemical migration

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1 **Abstract**

2 In multicomponent electrolyte solutions, the tendency of ions to diffuse at different rates results
3 in a charge imbalance that is counteracted by the electrostatic coupling between charged species
4 leading to a process called “electrochemical migration” or “electromigration”. Although not
5 commonly considered in solute transport problems, electromigration can strongly affect mass
6 transport processes. The number of reactive transport models that consider electromigration has
7 been growing in recent years, but a direct model inter-comparison that specifically focuses on the
8 role of electromigration has not been published to date. This contribution provides a set of three
9 benchmark problems that demonstrates the effect of electric coupling during multicomponent
10 diffusion and electrochemical migration and at the same time facilitates the inter-comparison of
11 solutions from existing reactive transport codes. The first benchmark (Lichtner, 1995) focuses on
12 the 1D-transient diffusion of HNO_3 ($\text{pH} = 4$) in a NaCl solution into a fixed concentration
13 reservoir, also containing NaCl - but with lower HNO_3 concentrations ($\text{pH} = 6$). The second
14 benchmark describes the 1D steady-state migration of the sodium isotope ^{22}Na triggered by
15 sodium chloride diffusion in neutral pH water. The third benchmark (Rolle et al., 2013) presents
16 a flow-through problem in which transverse dispersion is significantly affected by
17 electromigration. The system is described by 1D transient and 2D steady-state models. Very
18 good agreement on all of the benchmarks was obtained with the three reactive transport codes
19 used: CrunchFlow, MIN3P and PHREEQC.

20

21 **Keywords:** Reactive transport modeling, multicomponent diffusion, electromigration, model
22 intercomparison, benchmark

23 **1. Introduction**

24 It is well known that diffusive transport in multicomponent electrolyte systems cannot be fully
25 described by Fickian diffusion alone, but is affected by a variety of processes including the
26 electrostatic interactions between individual ions (Vinograd and McBain, 1941; Newman, 1973;
27 Ben-Yaakov, 1981; Cussler, 1997). Each dissolved species is subject to its own species-
28 dependent diffusion coefficient, affected by parameters such as charge and size of the ion
29 (Cussler, 1997) and ionic conductivity (Lasaga, 1979). As a result, dissolved species will tend to
30 diffuse at different rates, promoting the development of a charge imbalance in solution.
31 However, positively and negatively charged species are also affected by electric coupling, which
32 ensures that charge balance in solution is maintained. Generally speaking, “large” cations and
33 “small” anions are tied together electrostatically (Newman, 1973; Cussler, 1997) to enforce
34 electroneutrality at the macroscale - an essential condition in electrolyte solutions (Lichtner,
35 1996; Van Cappellen and Gaillard, 1996). This electric coupling leads to an additional mass
36 transport process called “electrochemical migration” or “electromigration” (Newman, 1991;
37 Ben-Yaakov, 1981). Fick’s law neglects these interactions, describes ion migration solely based
38 on concentration gradients, and consequently does not consider the electric field generated by
39 electrostatic bonding (coulombic interactions) of charged species (Lasaga, 1979; McDuff and
40 Ellis, 1979; Newman, 1991; Lichtner, 1996; Van Cappellen and Gaillard, 1996). In a
41 multicomponent system that includes charged species, diffusive ion migration is therefore better
42 described by the Nernst-Planck equation, a formulation that explicitly considers the electric
43 coupling between species and ensures the conservation of charge (Lasaga, 1979; McDuff and
44 Ellis, 1979; Newman, 1991; Lichtner, 1996; Van Cappellen and Gaillard, 1996; Boudreau et al.,
45 2004; Liu et al., 2011; Steefel et al., 2014).

46 In some cases, electrostatic interactions between diffusing species can have a strong
47 effect on ion mobility and can produce unexpected behavior such as uphill diffusion (e.g.:
48 Oelkers, 1996). In addition, apparent diffusion coefficients (i.e. diffusion coefficients derived
49 from Fick's law) may show a strong dependency on concentrations. Considering that the
50 quantification of diffusion coefficients is labor-intensive (Tyrell, 1961; Cussler, 1997), it is
51 impractical to determine apparent diffusion coefficients as a function of solution composition for
52 a range of conditions. Instead, it is advantageous to consider electrochemical interactions
53 affecting diffusion explicitly rather than lumping this effect into empirically measured apparent
54 diffusion coefficients.

55 Reactive transport models are commonly used for the quantitative investigation of flow,
56 transport and reaction processes in porous media. These models aid with the verification of
57 conceptual models, are used to design and evaluate experiments, and assist with the
58 interpretation of field data in the fields of geology, engineering and environmental research
59 (Boudreau, 1997; Kang et al. , 2006; Steefel et al., 2003; Wang and Van Cappellen, 1996;
60 MacQuarrie and Mayer 2005). Traditionally, diffusion has been implemented into reactive
61 transport models based on Fick's law and diffusion coefficients are often treated as adjustable
62 parameters (Cussler, 1997). However, the number of reactive transport models that include
63 electromigration and consider the chemical potential gradient as the driving force of diffusion
64 has been growing in recent years (Parkhurst and Appelo, 1999; Giambalvo et al., 2002; Shiba et
65 al., 2005; Johannesson et al 2007; Paz-Garcia et al., 2011; Muniruzzaman et al., 2014). Although
66 some aspects of electromigration on solute transport have been investigated (Oelkers, 1996;
67 Giambalvo et al., 2002; Steefel and Maher, 2009), a direct model inter-comparison that

68 specifically focuses on the role of electromigration and electrostatic effects on ion transport has
69 not been published to date.

70 This contribution was motivated by the need for benchmark problems suited to evaluate
71 the effect of electric coupling during multicomponent diffusion and electrochemical migration
72 and to facilitate an inter-comparison of existing reactive transport codes. The following
73 benchmark problems are specifically designed to highlight effects of electromigration. The first
74 two benchmarks are one-dimensional and the third benchmark includes two parts, involving one-
75 and two-dimensional scenarios. Three reactive transport codes were used independently for the
76 inter-comparison, namely CrunchFlow (Steefel et al., 2014), MIN3P (Mayer et al., 2002) and
77 PHREEQC (Parkhurst and Appelo, 1999).

78 **2. Governing Equations**

79 **Mass Transfer in Electrolytic Systems**

80 Species-specific diffusion is necessary to describe the behavior of electrolyte systems (Steefel
81 and Maher, 2009) where diffusive transport is the dominant mass transport process. The most
82 important feature that distinguishes the electrolyte systems from non-electrolyte systems is the
83 electric coupling of the ionic fluxes (Helfferich, 1962; Newman, 1973). In the electrolyte
84 systems, electric interaction of ion-ion, ion-solvent and ion-interface induces an electric field.
85 The treatment of electrolytic diffusion follows naturally from the generalized treatment of
86 diffusion (Taylor and Krishna, 1993).

87 **Nernst-Planck Equation for Multicomponent Systems**

88 The migration of interacting species is described by the Nernst-Planck equation, which can be
89 derived from expressions for the diffusive flux written in terms of the chemical potential (Steefel

90 et al, 2014). Written in terms of the flux of an arbitrary species i , the Nernst-Planck equation is
 91 given by:

$$92 \quad \mathbf{J}_i = -D_i \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{c_i F}{RT} z_i \nabla \psi \right) \quad (1)$$

93 where D_i is the species-dependent diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), c_i is the concentration (mol L^{-1}
 94 H_2O), γ_i is the activity coefficient (-), F is the Faraday constant (96485 C mol^{-1}), R is the gas
 95 constant ($8.341 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (K), z_i is the charge number (-) and ψ
 96 is the electric potential (V or J C^{-1}). In the presence of advection with a Darcy's velocity \mathbf{q} (m s^{-1}),
 97 the modified flux term is:

$$98 \quad \mathbf{J}_i = -D_i \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{c_i F}{RT} z_i \nabla \psi \right) + c_i \mathbf{q} \quad (2)$$

99 This expression is known as the extended Nernst-Planck equation and holds, in ideal systems, for
 100 all mobile species. It describes the movement of ions in a solution with or without external
 101 electric field (Helfferich, 1962, Bard, 1980 and Bagotsky, 2006). In a multicomponent system,
 102 the set of Nernst-Planck equations, one for each species, must be solved simultaneously.

103 By assuming small gradients in ionic strength, a dilute solution with low ionic strength
 104 and isothermal conditions, the contribution of the flux from the gradients in the logarithms of the
 105 activity coefficients can be neglected (Giambalvo et al., 2002; Steefel and Maher, 2009). With
 106 this approximation, the flux of an individual species becomes:

$$107 \quad \mathbf{J}_i = -D_i \left(\nabla c_i + \frac{c_i F}{RT} z_i \nabla \psi \right) + c_i \mathbf{q} \quad (3)$$

108 This equation represents the contributions of diffusion, electromigration and advection to the
 109 total mass transfer. Assuming there is no externally induced current (null current assumption), a
 110 simplified version of the mass flux can be derived (Giambalvo et al., 2002):

111
$$\mathbf{J}_i = -D_i \left(\nabla c_i + c_i z_i \frac{\mathbf{q} \sum_j^{N_{aq}} z_j c_j - \sum_k^{N_{aq}} D_k z_k \nabla c_k}{\sum_l^{N_{aq}} D_l z_l^2 c_l} \right) + c_i \mathbf{q} \quad (4)$$

112 This formulation has the advantage that the electric potential does not appear as a primary
 113 unknown and is therefore well suited for implementation in standard reactive transport codes.

114 **3. Participating Codes**

115 The three reactive transport codes participating in this benchmarking exercise are CrunchFlow
 116 (Steeffel et al., 2014), MIN3P (Mayer et al., 2002) and PHREEQC (Parkhurst and Appelo, 1999).
 117 CrunchFlow and MIN3P are 3D block-centered finite difference (finite volume) models using
 118 the global implicit approach (GIA) to solve the fully coupled transport and reaction equations.
 119 PHREEQC solves the multicomponent diffusion problem with a 1D finite difference method
 120 using the sequential non-iterative approach (SNIA). A detailed description of the formulation
 121 and capabilities of the codes is discussed elsewhere (Steeffel et al., 2014 and references therein).
 122 PHREEQC considers the gradients of the activity coefficients in its implementation (Appelo and
 123 Wersin, 2007) whereas CrunchFlow and MIN3P neglect this contribution.

124 **4. Benchmark Descriptions**

125 The three benchmark problems are summarized in **Table 1**. The first benchmark (Benchmark 1)
 126 focuses on the role of electromigration in driving the flux of the various charged species to
 127 maintain local charge balance and was first presented by Lichtner (1995). This problem
 128 considers diffusion of HNO_3 from a low pH solution ($\text{pH} = 4$) into a circum-neutral reservoir (pH
 129 $= 6$) with low HNO_3 concentrations, both with the same elevated NaCl background
 130 concentrations.

131

132 **Table 1.** Summary of multicomponent diffusion benchmarks

| Benchmark | Description | Processes | Dimension |
|------------------|---|--|------------------|
| 1 | HNO ₃ (pH 4) diffusion into a circum-neutral pH reservoir | Diffusion/Electromigration | 1D |
| 2 | Sodium isotope fractionation induced by sodium chloride diffusion in neutral pH water | Diffusion/Electromigration | 1D |
| 3 | Transverse dispersion affected by electromigration | Advection/Diffusion/ Electromigration | 1D/2D |

133

134 The second benchmark (2) shows the electromigration and subsequent fractionation of the
135 sodium isotope ²²Na⁺ due to diffusion of NaCl under neutral pH conditions. The problem is
136 loosely based on Glaus et al (2013); however, the benchmark case presented here is set up for a
137 uniform relatively coarse-grained uncharged porous medium and does not include diffusion
138 through charged micropores as would be the case if porous clay were considered. In the first two
139 benchmarks, diffusion and electromigration are the only transport processes and models are set
140 up in one dimension. The third benchmark (3) investigates the effect of electromigration on
141 transverse dispersion and is based on experiments and modeling carried out by Rolle et al.
142 (2013). This benchmark also includes advection and is characterized by a higher level of
143 complexity; it is simulated in one- and two-dimensions.

144 **Benchmark 1: Transient Electromigration**

145 This problem was initially presented by Lichtner (1995) and has previously been used as an
146 example to illustrate the multicomponent capabilities of PHREEQC (Appelo, 2007). It is a 1D
147 transient problem with a fixed concentration (Dirichlet) boundary condition on the left (at $x = 0$),

148 representing the reservoir, and a no-flux (Neumann) boundary condition on the right ($x = 0.01$
 149 m). The chemical system is composed of four primary (component) species (H^+ , NO_3^- , Na^+ and
 150 Cl^-) and one secondary species (OH^-). The porosity is set to 1.0 and the domain is discretized
 151 into 100 equally spaced cells of 100 microns each. The temperature is 25°C and there is no flow,
 152 the only transport process is multicomponent diffusion according to the Nernst-Planck equation.
 153 Activity coefficients are calculated with the extended Debye-Hückel equation. Species-
 154 dependent diffusion coefficients, as well as the initial and boundary conditions defining the
 155 chemical system are given in **Table 2**.

156

157 **Table 2.** Boundary conditions, initial conditions, and species dependent diffusion coefficients for
 158 Benchmark 1 (transient electromigration problem).

| Species | Boundary Condition (mM) | Initial Condition (mM) | Diffusion Coefficient ($m^2 s^{-1}$) |
|----------|------------------------------------|------------------------------------|--|
| pH | 6.001 | 4.007 | 9.31×10^{-9} |
| Na^+ | 0.1 | 0.1 | 1.33×10^{-9} |
| Cl^- | 0.1 | 0.1 | 2.03×10^{-9} |
| NO_3^- | 0.001 | 0.1 | 1.90×10^{-9} |
| OH^- | ^a 1.03×10^{-5} | ^a 1.06×10^{-7} | 5.27×10^{-9} |

159 ^a OH^- concentrations are only provided for completeness, calculated from H^+ and H_2O ($K_w = 10^{-14}$)

160

161 The problem is run for 1 hour using a constant time step of 0.001 hour (corresponding to 1,000
 162 time steps). Results are compared along the spatial profile after $T = 1$ hour for H^+ , Na^+ , NO_3^- and
 163 Cl^- .

164 **Benchmark 2: Tracer Isotope Diffusion**

165 This 1D problem involves three primary (component) species, Na^+ , Cl^- , and H^+ , along with an
 166 isotope of Na that is also treated as a distinct component, $^{22}Na^+$. In addition, a single secondary
 167 species, OH^- , is considered. In this case, fixed concentration (Dirichlet) boundary conditions are
 168 considered at either end of the domain. The initial condition in the domain is divided into two

169 regions; concentrations in half of the domain are equivalent to those at the left boundary, while
 170 concentrations in the other domain half are defined by the right boundary condition. However,
 171 the initial conditions are not significant since the simulation is run until steady state conditions
 172 are achieved. The porosity is set to a constant and uniform value of 0.5 and the domain is
 173 discretized into 100 equally spaced cells of 100 microns each. The diffusion coefficients of Na^+
 174 and $^{22}\text{Na}^+$ are assumed to be identical. A constant time step of 1 hour is used and the simulation
 175 is run to 1,500 days to ensure that steady-state is achieved. Concentrations at the boundaries and
 176 species-dependent diffusion coefficients are described in **Table 3**. The simulation also assumes
 177 no flow.

178
 179 **Table 3.** Boundary conditions and diffusion coefficients for Benchmark 2 (isotope tracer problem).

| Species | Left Boundary Condition (mM) | Right Boundary Condition (mM) | Diffusion Coefficient ($\text{m}^2 \text{s}^{-1}$) |
|--------------------|------------------------------------|------------------------------------|--|
| pH | 7.0 | 7.0 | 9.31×10^{-9} |
| Na^+ | 0.5 | 0.1 | 1.33×10^{-9} |
| $^{22}\text{Na}^+$ | 10^{-6} | 10^{-6} | 1.33×10^{-9} |
| Cl^- | 0.5 | 0.1 | 2.03×10^{-9} |
| OH^- | ^a 1.05×10^{-4} | ^a 1.03×10^{-4} | 5.27×10^{-9} |

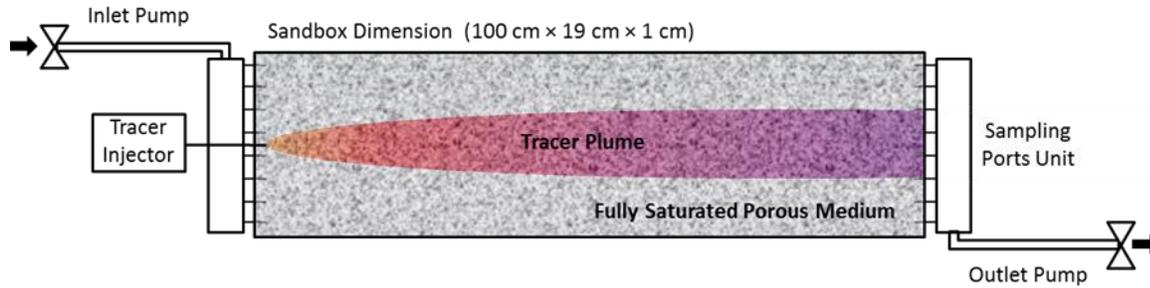
180 ^aOH⁻ concentrations are only provided for completeness, calculated from H⁺ and H₂O ($K_w = 10^{-14}$)

181

182 **Benchmark 3: Transverse Dispersion**

183 Rolle et al. (2013) investigate the effect of electromigration on transverse dispersion under
 184 steady state flow conditions. In the full 2D case, the problem involves unidirectional flow and
 185 transport of a multicomponent tracer plume down the length of a 2D flow-through chamber.

186



187

188 **Figure 1.** Schematic of the 2D flow and transverse dispersion experiment conducted by Rolle et al.
 189 (2013).

190

191 Using PHREEQC, Rolle et al. (2013) solved the problem numerically by simulating transverse
 192 dispersion and electromigration perpendicular to the flow path as a 1D problem. This approach
 193 simplifies a 2D steady-state problem into a 1D transient problem by making use of the
 194 transformation $t = x/v$, where x is the distance from the source for the 2D problem, v is the
 195 uniform average linear groundwater velocity, and t defines the travel time to reach the location x .
 196 At the same time, t defines the simulation time for the 1D transient transverse dispersion problem
 197 (Rolle et al., 2013). Coinciding with experimental conditions, a 1 cm source in the middle of the
 198 12 cm wide cross section at $x = 0$ describes the continuous release of the electrolyte solution. The
 199 simulation was run for the case of an average linear velocity of 1.5 m day^{-1} . The results of the
 200 1D transient simulations are compared among the three participating codes, whereas fully 2D
 201 simulations with explicit treatment of flow were performed with CrunchFlow and MIN3P.

202

203 **Table 4.** Chemical conditions and transverse dispersion coefficients for Benchmark 3 (transverse
 204 dispersion problem).

| Species | Tracer Injection Ports (mM) | Initial Condition (1D) and Remaining Injection Ports (2D) (mM) | Diffusion Coefficient ($\text{m}^2 \text{s}^{-1}$) | Transverse Dispersion Coefficient ($\text{m}^2 \text{s}^{-1}$) |
|------------------|-----------------------------|--|--|--|
| K^+ | 0.29 | 10^{-6} | 1.77×10^{-9} | 2.405×10^{-9} |
| Mg^{2+} | 0.29 | 10^{-6} | 6.26×10^{-10} | 1.745×10^{-9} |
| Cl^- | 0.87 | 3×10^{-6} | 1.81×10^{-9} | 2.425×10^{-9} |

205

206 The dispersion coefficients used in these simulations require some discussion. In fact, the
207 parameterization of the hydrodynamic transverse dispersion coefficient used in Rolle et al.
208 (2013) differs from the classical linear model commonly adopted in subsurface applications of
209 solute transport and reads as:

$$210 \quad D_i^T = D_i^P + D_i^{aq} \left(\frac{Pe^2}{Pe + 2 + 4\delta^2} \right)^\beta \quad (5)$$

211 where D_i^P is the pore diffusion coefficient approximated as the product of the aqueous diffusion
212 coefficient of a species i and the porosity of the medium (0.41). $Pe=vd/D_i^{aq}$ is the grain Péclet
213 number where d is the average grain size (1.25 mm). $\delta=6.2$, and $\beta=0.47$ are empirical parameters
214 determined in previous multitracer experiments and pore-scale simulations (Rolle et al., 2012).
215 Equation 7 explicitly retains a direct dependence of the mechanical dispersion term on the
216 aqueous diffusivity of the transported species; the non-linear dependence on the average flow
217 velocity arises from the incomplete mixing in the pore channels (e.g. Hochstetler et al., 2013;
218 Rolle and Kitanidis, 2014).

219 For this benchmark analysis we considered the mixed electrolyte case described in Rolle et al.,
220 2013, where a dilute solution of KCl and MgCl₂ was continuously injected in ambient deionized
221 water. The free aqueous diffusion coefficients of the ions at T=20 °C are $D_{K^+} = 1.77 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$,
222 $D_{Mg^{2+}} = 6.26 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and $D_{Cl^-} = 1.81 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. These values used in Eq. 7 yield the
223 transverse dispersion coefficients given in the last column of **Table 4**.

224 **1D Benchmark:** The 1D benchmark consists of a pure transverse diffusion problem discretized
225 into 48 grid cells of 2.5 mm. In the 1D system, the injection ports constitute initial conditions
226 used at grid cells 23-26, corresponding to a 10 mm wide region in the center of the symmetrical

227 system. The initial condition is used everywhere else in the domain and is intended to represent
228 deionized water. The transverse dispersion coefficients given in **Table 4** are used. The
229 boundaries at either end of the system are treated as no-flux, but they do not influence the system
230 behavior for the 16 hour simulation time (corresponding to $x = 1$ m, i.e. the outflow boundary of
231 the domain). The simulation was run with a constant 0.001 hour time step.

232 **2D Benchmark:** For the full 2D problem solved with CrunchFlow and MIN3P, the transverse
233 discretization is 50 grid cells with a spacing of 2.4 mm (corresponding to a total width of 0.12
234 m). At the inlet boundary, grid cells 24, 25, 26 and 27 in the transverse direction are set at the
235 tracer injection port concentrations of 0.29 mM K^+ , 0.29 mM Mg^{2+} , and 0.87 mM Cl^- (see
236 **Table 4**), while the remaining injection ports carry deionized water. The longitudinal
237 discretization is 500 grid cells with a spacing of 2.4 mm thus a total length of 1.2 m; the
238 concentrations are reported at $x = 1.0$ m, corresponding to the outflow boundary of the
239 experimental setup. The additional length of 0.2 m is considered in the models to avoid any
240 possible boundary effects. In this case, lateral flow can be calculated, or simply prescribed at 1.5
241 $m\ day^{-1}$. A maximum time step of 1 hour is used with an initial minimum time step of 10^{-6} hours.
242 The simulation time is 32 hours to ensure that the final results correspond to steady state
243 conditions representative of the experiment.

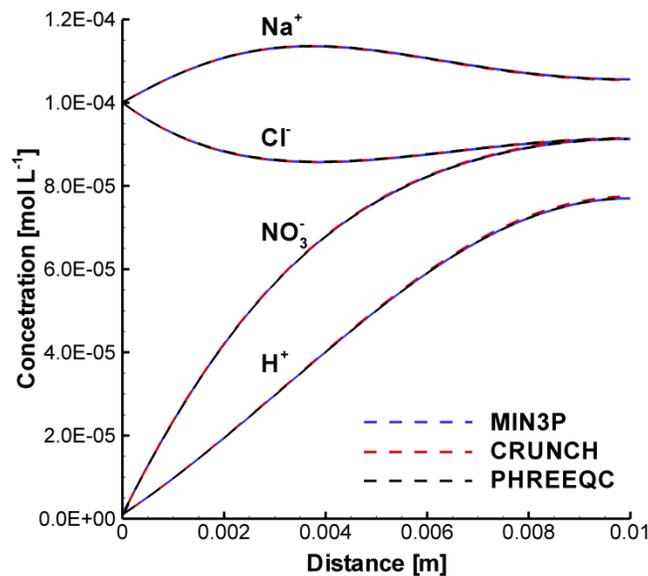
244 **5. Results and Discussion**

245 **Benchmark 1**

246 Simulation results for the Benchmark 1 (Lichtner, 1995) depict the diffusion of HNO_3 ($pH =$
247 4.007) from the solution domain towards the boundary where NO_3^- concentration are 100 times
248 lower and $pH = 6.001$. Results for NO_3^- and H^+ reveal that both ions continue to diffuse towards

249 the left boundary after 1 hour simulation time (**Figure 2**). Because the diffusion coefficient for
250 H^+ is much larger than the corresponding value for NO_3^- , H^+ has become substantially more
251 depleted in the domain than NO_3^- . The discrepancy in diffusion rates of H^+ and NO_3^- triggered
252 electromigration of Na^+ and Cl^- to maintain local charge balance; Na^+ is entering the domain to
253 offset the preferential loss of H^+ , while Cl^- is leaving the system to counterbalance NO_3^- , which
254 is preferentially retained. Migration of Na^+ and Cl^- occurs despite the fact that there was no
255 initial concentration gradient of either species (**Table 2**) and takes place even against the
256 developing concentration gradients of Na^+ and Cl^- . If Fick's Law were used to describe this
257 multispecies diffusion problem, there would be no change in Na^+ and Cl^- concentration and
258 consequently electroneutrality would be violated.

259 There is very good agreement between the simulation results of all three codes and they
260 demonstrate near identical outputs. Simulations were executed on a desktop computer equipped
261 with an Intel Core 2 Quad CPU with two 2.4 GHz processors, 8 GB RAM and a 64-bit operating
262 system.



263
264

265 **Figure 2:** Species concentrations after 1 hour simulation time for HNO₃ diffusion (Benchmark 1). The
266 left boundary is a fixed concentration (Dirichlet) boundary, while the right boundary is no-flux.

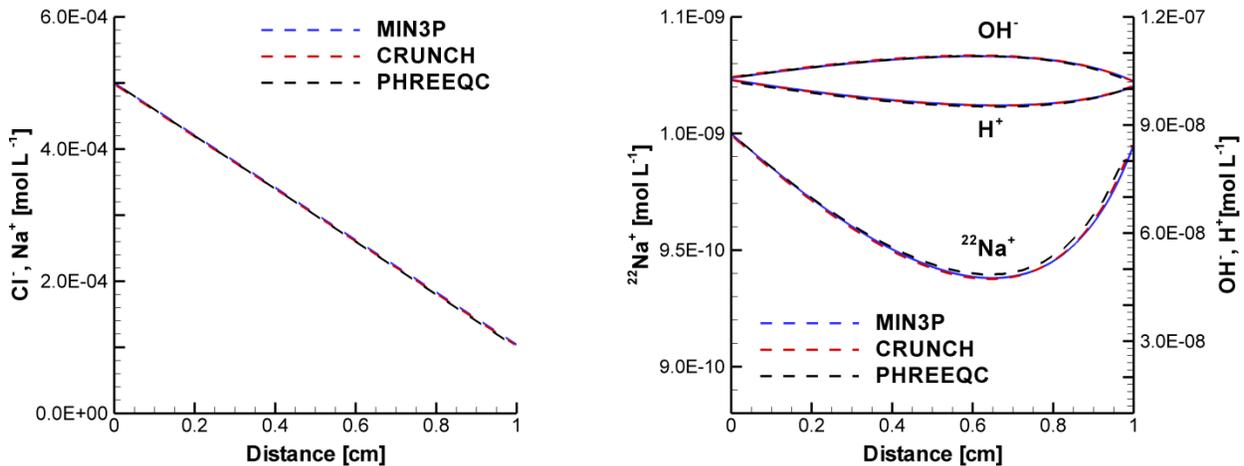
267

268 **Benchmark 2**

269 The results of the Benchmark 2 simulation visually show steady state diffusion with same
270 concentration profiles for Na⁺ and Cl⁻ from left to right (

271 **Figure 3**). However, it has to be kept in mind that the diffusion coefficient for Cl⁻ is considerably
272 larger than the one for Na⁺. In fact, considering that the equations are based on the null current
273 assumption, this holds back Cl⁻ migration and accelerates Na⁺ migration. Although there are no
274 initial concentration gradients for ²²Na⁺, H⁺ and OH⁻, these species, present at much lower
275 concentrations, also become affected by the electrostatic coupling.

276



277
278

279 **Figure 3:** Na⁺, Cl⁻, H⁺, OH⁻ and ²²Na⁺ concentrations after 1500 days for system summarized in Table 2
280 (Benchmark 2). The left boundary is a fixed concentration (Dirichlet) boundary at 0.5 mM, while the
281 right boundary is a fixed concentration boundary at 0.1 mM for Na⁺, Cl⁻. The fixed gradient in NaCl
282 results in a flux of H⁺, OH⁻ and ²²Na⁺, despite the fact that their concentrations are the same at either end
283 of the column.

284

285 A closer look at the results reveals that H^+ migrates from the left to the right to enhance the
286 positive charge flux, while OH^- migrates from the right to the left to counteract the negative
287 charge flux from the left to the right dominated by Cl^- . Primarily, one would expect that $^{22}Na^+$
288 should also be subjected to a net flux from the left to the right; however, the sodium isotope is
289 present at very low concentrations and is more strongly affected by migration dynamics of H^+
290 and OH^- , resulting in a net migration from the right to the left inducing an unexpected isotope
291 fractionation. Solving this problem with Fick's law would not predict $^{22}Na^+$ isotope fractionation,
292 H^+ and OH^- migration, and would result in a net negative charge flux across the domain. These
293 results suggest that multicomponent diffusion can introduce isotope fractionation, even in the
294 absence of fractionating reactions.

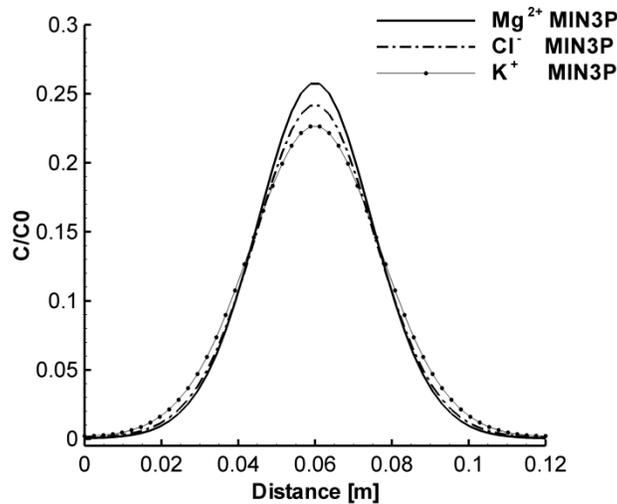
295 Overall, there is very good agreement between the three codes with better agreement between
296 CrunchFlow and MIN3P. Slight differences are observed for the PHREEQC results. It is difficult
297 to decisively determine the reasons for these differences, but it is likely that the discrepancies are
298 due to slight variations in model formulation (i.e. consideration of activity gradients in the
299 PHREEQC formulation, absent in the other two codes) and/or the use of different coupling
300 schemes (GIM vs. SNIA). However, all codes show identical trends and concentration
301 differences are small, implying that the residual discrepancies will not affect the interpretation of
302 the results.

303

304 **Benchmark 3: 1D Transverse Dispersion**

305 The transverse concentration profiles for Cl^- , K^+ and Mg^{2+} are plotted at the outlet ($x = 1.0$ m)
306 corresponding to a residence time of 16 hours in the 2D domain. The separation of the three
307 tracer profiles (

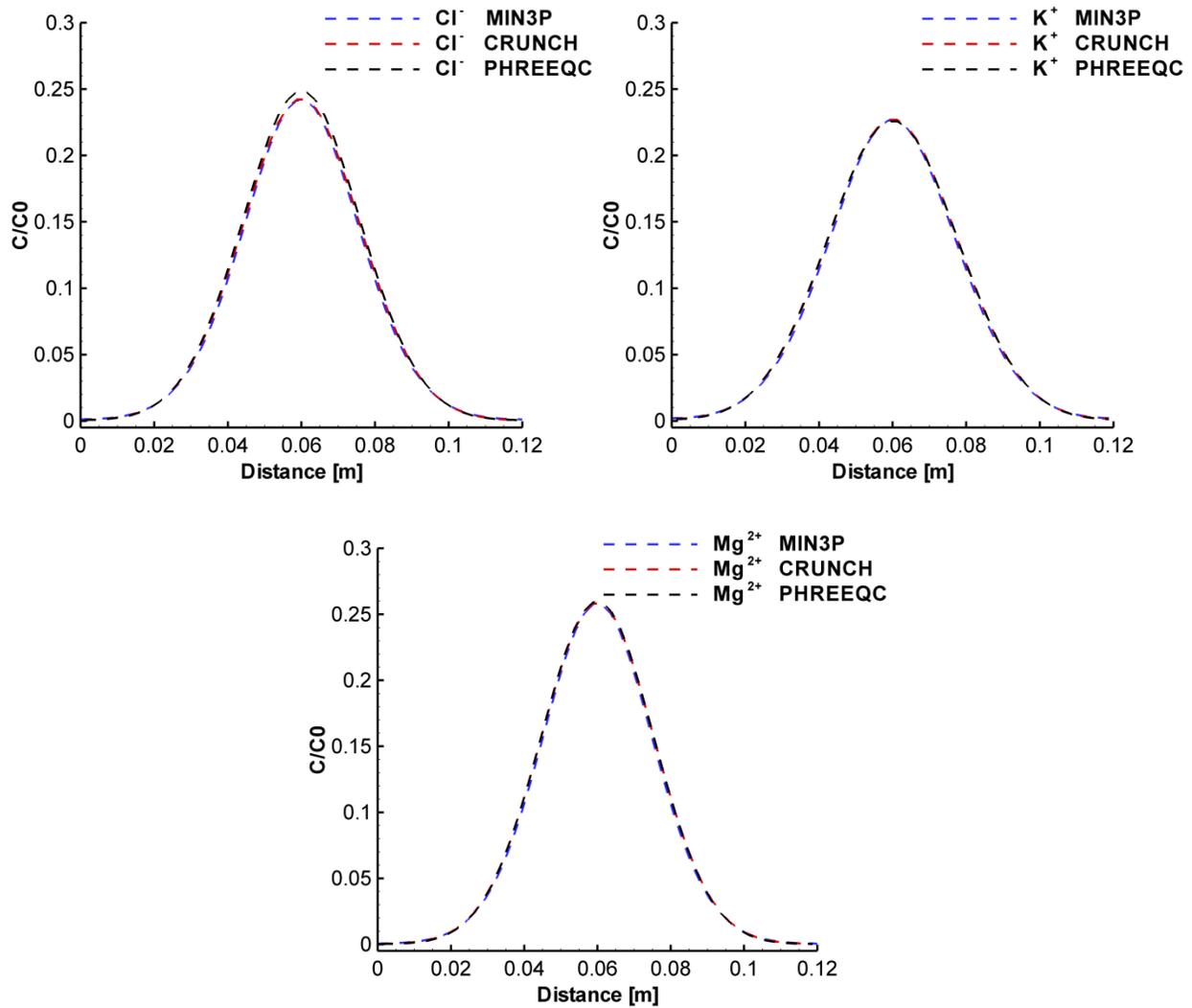
308 **Figure 4)** demonstrates the effect of species-dependent dispersion coefficients and
 309 electrochemical migration on transverse displacement. The Cl^- concentration profile is located
 310 between K^+ and Mg^{2+} despite having the largest diffusion coefficient. In fact, D_{Cl^-} in liberated
 311 state is considerably larger than $D_{\text{Mg}^{2+}}$ and also slightly larger than D_{K^+} (**Table 4**). These results
 312 show that Cl^- migration is retarded due to electrostatic coupling with the cations and in particular
 313 with Mg^{2+} , which diffuses more slowly. The outcomes reported in Fig. 4 demonstrate the
 314 positive contribution of electromigration to transverse displacement of the two cations and the
 315 negative contribution of electromigration to transverse displacement of chloride (Rolle et al.,
 316 2013).



317
 318
 319 **Figure 4.** 1D simulation results of transverse profiles for Cl^- , K^+ and Mg^{2+} at the outlet (corresponding to
 320 a residence time of 16 hours) demonstrate the effect of species-dependent dispersion and electromigration
 321 on the transverse displacement of charged species (1D Benchmark 3 solved with MIN3P).

322
 323 There is a very good agreement between the three codes and an excellent match between
 324 CrunchFlow and MIN3P (

325 **Figure 5).** Similar to the two previous benchmarks, there are slight differences between the
 326 results of CrunchFlow and MIN3P on the one hand and PHREEQC on the other hand. Peak
 327 chloride concentrations predicted by PHREEQC are slightly higher than those calculated by
 328 CrunchFlow and MIN3P (~ 0.6%). Magnesium and potassium concentration profiles are in very
 329 good agreement for all codes.

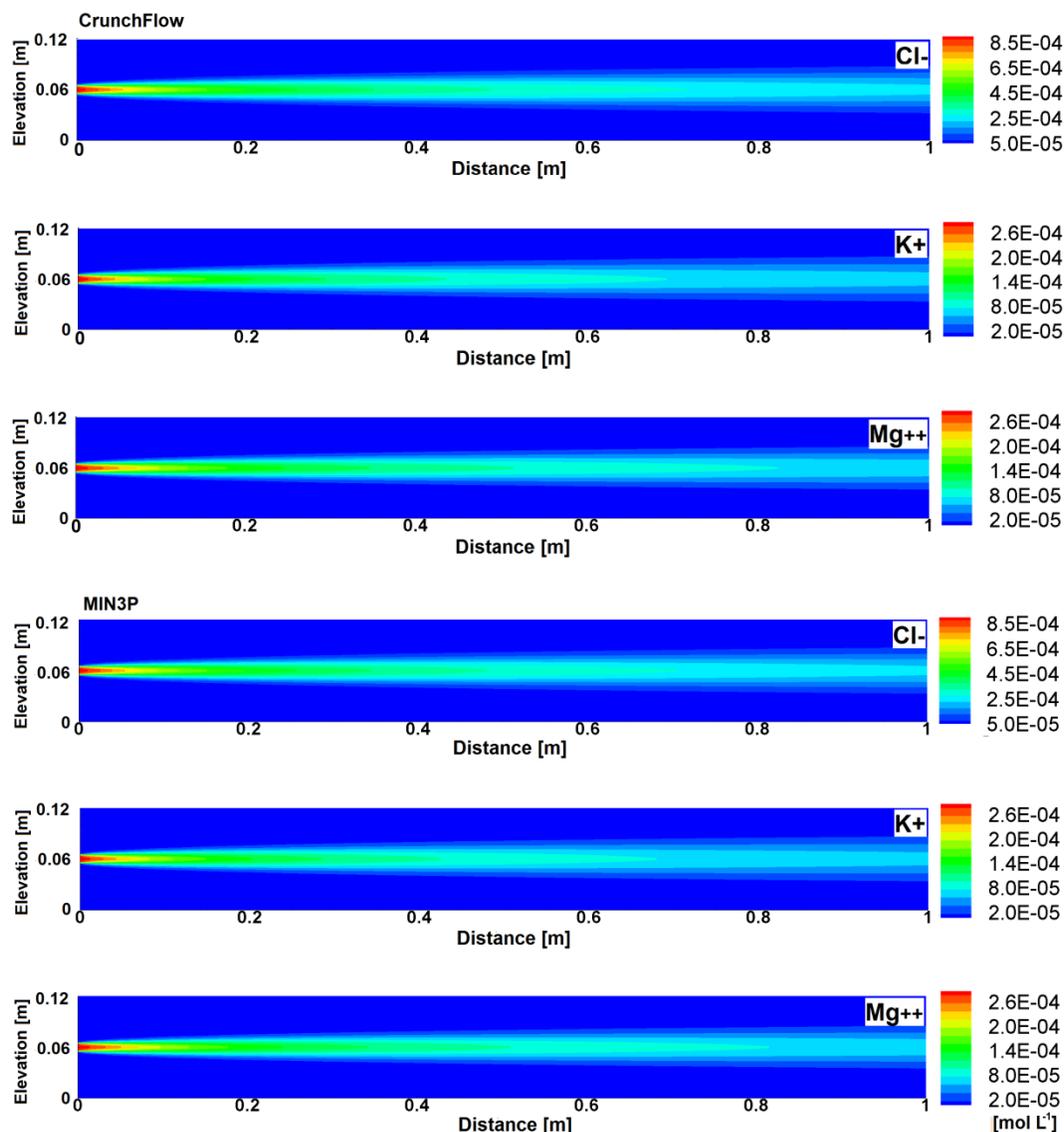


333 **Figure 5.** 1D simulation of transverse multicomponent diffusion for the case of transport of mixed
 334 electrolytes (KCl and MgCl₂ solution) in pure water described by Rolle et al. (2013), comparing
 335 CrunchFlow, MIN3P and PHREEQC results.

336

337 **Benchmark 3: 2D Flow and Transverse Dispersion**

338 Using CrunchFlow and MIN3P it was possible to carry out a full two-dimensional flow and
339 multicomponent transport simulation of the flow-through system. The simulation was run for
340 two pore volumes (32 hours) to ensure that steady state conditions at the outflow were reached.
341 To illustrate the 2D concentration distributions and to provide a means for visual comparison of
342 the CrunchFlow and MIN3P results, 2D contour plots are provided for K^+ , Mg^{2+} and Cl^- (**Figure**
343 **6**).



344

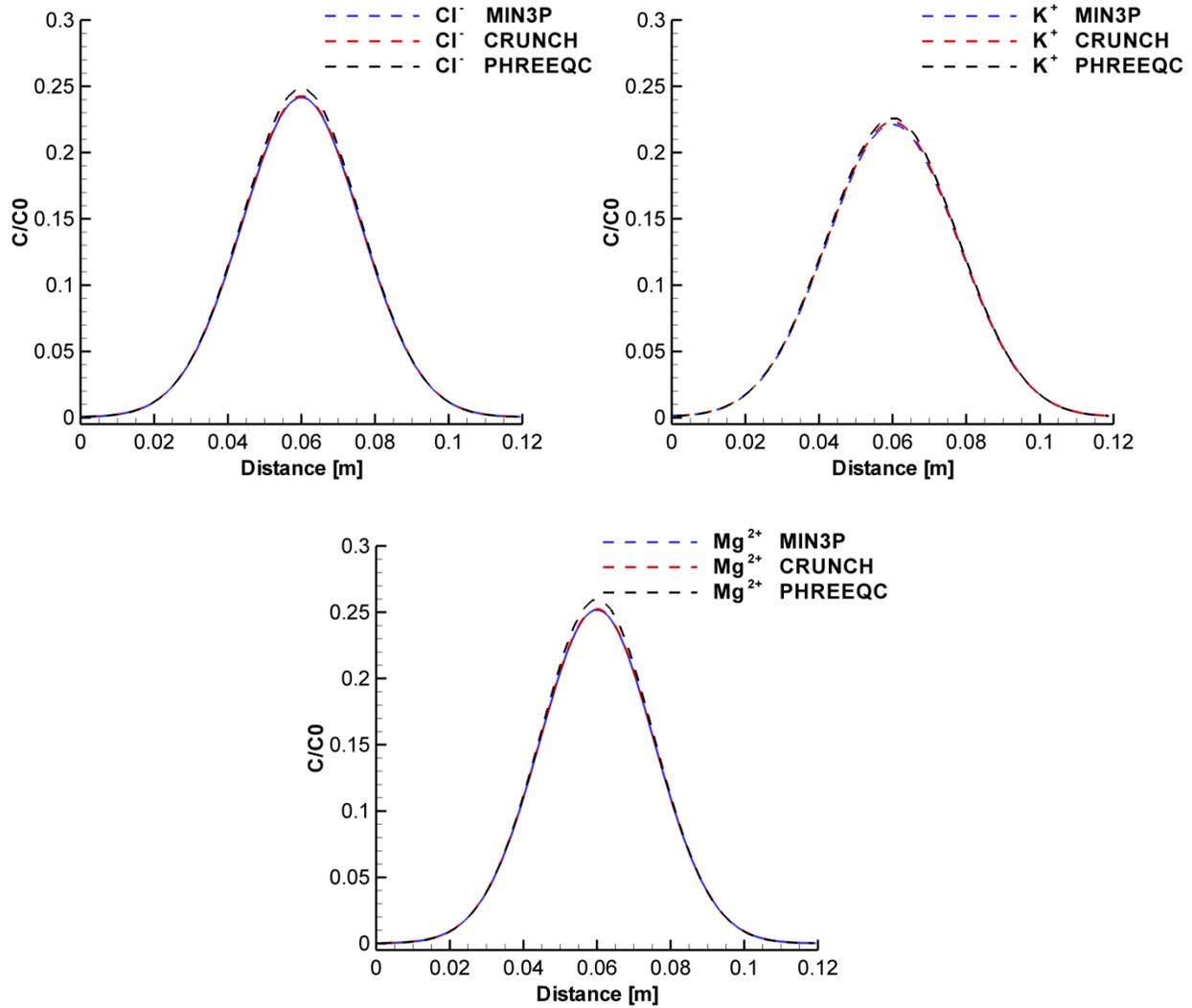
345

346 **Figure 6.** Simulation results for Benchmark 3 considering flow (uni-directional) and multicomponent
 347 transverse dispersion for steady-state conditions, from top to bottom are shown: K^+ , Mg^{2+} and Cl^- for
 348 CrunchFlow and K^+ , Mg^{2+} and Cl^- for MIN3P.

349

350 Cross-sections extracted from two-dimensional steady state CrunchFlow and MIN3P results are
 351 compared at the outflow to one-dimensional transient PHREEQC results, corresponding to a
 352 residence time of 16 hours. Overall, there is an excellent agreement between MIN3P and
 353 CrunchFlow results (**Figure 7**) and results are also very close to the concentrations computed with the
 354 1D PHREEQC approach. PHREEQC concentration profiles are slightly higher than CrunchFlow

355 and MIN3P (the differences of the peak concentrations are ~ 0.6% for Cl^- , ~ 0.7% for Mg^{2+} and
356 ~ 0.4% for K^+).



358

359 **Figure 7.** Comparison of 1D PHREEQC results (no explicit consideration of flow, only following the
360 plume as it moves down the flow path) and transverse profiles derived from 2D CrunchFlow and MIN3P
361 runs for the transverse dispersion problem. The CrunchFlow 2D runs are based on GIMRT and use a first
362 order upwind formulation, along with a backwards Euler time stepping approach, the same numerical
363 methods are used in the MIN3P simulations.

364

365 **6. Concluding Remarks**

366 Three benchmark problems were presented, each with significant effects of multicomponent
367 diffusion and electromigration on transport of solutes in saturated porous media. The
368 benchmarks were specifically designed to be sensitive to the effect of electromigration on
369 diffusion and lateral concentration displacement. Benchmarks 1 and 2 are hypothetical problems
370 that provide opportunities to verify the implementation of multicomponent diffusion and
371 electromigration formulations in reactive transport codes. Benchmark 3 is based on the outcomes
372 of laboratory experiments (Rolle et al., 2013) and provides the opportunity to verify and validate
373 multicomponent diffusion and species-dependent transverse dispersion formulations under flow-
374 through conditions. Three reactive transport codes with the capability of simulating
375 multicomponent diffusion and electrochemical migration participated in this study (CrunchFlow,
376 MIN3P and PHREEQC). For all benchmark problems considered in this work an overall very
377 good agreement between the simulation results obtained with the different codes. Despite some
378 residual discrepancies between the simulation results, all three codes were able to consistently
379 reproduce the same trends and evolution in concentration patterns induced by multicomponent
380 diffusion and by the electrostatic interactions between the charged species. Small discrepancies
381 between the results indicate that different approaches in implementing the governing equations
382 are not a significant source of uncertainties for model applications; uncertainties will rather be
383 dominated by the underlying conceptual model.

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392

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