GEOQuébec 2015
Challenges from North to South
Des défis du Nord au Sud

# Modelling of elution tests with the iCP interface between COMSOL and Phreeqc

François Duhaime, Céline Rep & Jean-Sébastien Dubé
*Laboratory for Geotechnical and Geoenvironmental Engineering (LG2)*
*École de technologie supérieure, Montreal, Canada*

## ABSTRACT

The iCP interface allows the coupling of Phreeqc, a geochemical modelling code, and COMSOL, a finite element solver, for the modelling of reactive transport in soils. With the iCP interface, the equations describing the transport of chemical species in pore water are first solved in COMSOL. The updated chemical analyses for each cell are then sent to Phreeqc for thermodynamic equilibrium and kinetics calculations. In this paper, the iCP interface was tested by modelling a series of laboratory tests conducted with a natural soil (calcareous sand). These tests included a batch test where a solution of lead, copper, cadmium and zinc nitrates was put in contact with the soil, a conservative tracer test with bromide and an elution test with the same metal nitrates as for the batch test. For the batch and elution tests, Phreeqc was used to model the dissolution of calcite in the soil and the precipitation of metal carbonates. COMSOL was used to model solute transport for the tracer and elution tests. This paper is centered on a coupling between hydrodynamic and geochemical phenomena, but the iCP interface could also be applied to multiphysics models involving mechanical (e.g., cementation) and thermal (e.g., heat produced by chemical reactions) equations.

## RÉSUMÉ

L’interface iCP permet de coupler Phreeqc, un code de modélisation géochimique, et COMSOL, un solveur d’éléments finis, pour la modélisation du transport réactif dans les sols. Avec l’interface iCP, les équations décrivant le transport des espèces chimiques dans l’eau interstitielle sont tout d’abord résolues avec COMSOL. Les analyses chimiques pour chaque cellule sont ensuite transmises vers Phreeqc pour des calculs d’équilibre thermodynamique et de cinétique. Dans cet article, l’interface iCP a été testée en modélisant une série d’essais en laboratoire réalisés avec un sol naturel (sable calcaire). Ces essais incluent un essai en bécher durant lequel une solution de nitrates de plomb, cuivre, cadmium et zinc a été mise en contact avec le sol, un essai de traçage au bromure et un essai d’élution avec les mêmes nitrates de métaux qui ont été utilisés pour l’essai en bécher. Pour l’essai en bécher et l’essai d’élution, Phreeqc a été utilisé pour modéliser la dissolution de la calcite et la précipitation des carbonates de métaux. COMSOL a été utilisé pour modéliser le transport des espèces dissoutes pour l’essai de traceur et l’essai en bécher. Cet article est centré sur un couplage entre des phénomènes hydrodynamiques et géochimiques, mais l’interface iCP pourrait aussi être utilisée pour des modèles couplés impliquant des équations mécaniques (ex. cimentation) et thermiques (ex. chaleur produite par des réactions chimiques).

## 1 INTRODUCTION

Multiphysics models have become increasingly common in the past 20 years. In hydrogeology and geotechnical engineering, multiphysics models often concentrate on THM simulations, those that combine the modelling of thermal, hydrodynamic and geomechanical phenomena (or physics in the COMSOL terminology). The TOUGH family of codes is a relatively well known example of THM models (Finsterle et al. 2014). It was developed for the study of geothermal reservoirs and it has been used for the modelling of geological repositories for nuclear wastes, two important sources of impetus for the development of multiphysics models in earth sciences and geotechnical engineering.

COMSOL is another example of multiphysics code. It is best described as a finite-element solver for custom sets of coupled differential equations. It allows the user to program his differential equations or choose differential equations from a series of preprogrammed interfaces. One important COMSOL feature is its JAVA and MATLAB programming interfaces. These allow COMSOL simulations to be included in MATLAB scripts or JAVA classes. Application examples for the programming interfaces include extended parametric studies and post-processing in MATLAB (Bélisle 2013), and the application of unusual boundary conditions on models (Duhaime and Chapuis 2014).

The JAVA programming interface also allows COMSOL to be linked with other codes, thus extending its multiphysics capabilities. Nardi et al. (2014) programmed an interface between COMSOL and Phreeqc, a geochemical modelling code (Charlton and Parkhurst 2011). With this interface, COMSOL is used to model variably saturated groundwater seepage and other COMSOL physics if necessary (thermal, geomechanics, etc.), while Phreeqc uses a geochemical database to calculate thermodynamic equilibria, speciation, surface interactions and reaction kinetics. In effect, iCP allows Phreeqc models to be coupled with any sets of differential equations.

A very limited number of iCP applications have been presented in the literature thus far. The main objective of the paper is to show how iCP can be used to put geochemical models and hypothesis to the test. Experimental results presented by Dubé (2001) are used to develop an exploratory iCP model. The geochemical model is partly based on a Phreeqc model created by Lassabatère et al. (2007) for similar tests. Dubé (2001) studied the interaction between a calcareous soil and metals (Pb, Cu, Zn and Cd) using two types of tests: a batch test where metal nitrate solutions were put in contact with the soil, and an elution test with the same metal solution which also involved conservative tracer elution tests with bromide. With respect to the iCP interface, these tests have the advantage of isolating geochemical processes with the batch test, hydrodynamic processes with the tracer tests, and combining them with the elution tests.

The paper begins with a short description of the Dubé (2001) tests and of the findings presented by Lassabatère et al. (2007) for similar experiments. A presentation of the three numerical modelling steps follows (Phreeqc, COMSOL and iCP). Numerical and experimental results are then compared.

It should be noted that the numerical model presented in this paper is exploratory and could have been programmed entirely through Phreeqc because the soil was saturated and because of the simple advection-dispersion model that was used (e.g., Réginensi 2009). Examples of model improvement that would take advantage of the iCP features and the Lassabatère et al. (2007) geochemical model are given in the discussion.

## 2 BATCH AND ELUTION TESTS

The main objective behind the work of Dubé (2001) was to get a better understanding of the migration of metals in soils showing preferential flow pathways. To do so, Dubé (2001) conducted several tracer and metal elution tests with variable proportions of water and air occupying the soil pore volume.

The portion of a natural calcareous sand passing the 10 mm sieve was used by Dubé (2001) for most of his experiments. The sand identified as IDA (for L'Isle d'Abeau, a commune in the urban region of Lyon, France), has been featured in several other research projects (e.g., Plassard et al. 2000; Lassabatère et al. 2007) and is well characterized. The material passing the 10 mm sieve had $d_{10}$ and $d_{60}$ values of respectively 0.04 and 0.5 mm where $d_{10}$ and $d_{60}$ are the grain sizes for which respectively 10% and 60% of the soil mass is smaller. The solid carbonate content of the IDA sand was 16% (w/w). It had an organic matter content of 1.75% (w/w) and a cation exchange capacity of 27.5 meq/kg of soil.

Results from the batch test and two elution tests from Dubé (2001) were selected to test the iCP interface and are described below. The two selected elution tests were conducted in saturated soil columns. It should be noted that iCP can handle multiphase flow (unsaturated flow, or three-phase flow with an organic phase, water and air), but that it was decided to start with a relatively simple problem to experiment with the interface.

The batch test consisted of a series of 39 soil suspensions prepared with 10 mL of a solution of metal nitrates ($Cd(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$ and $Cu(NO_3)_2$) and 1 g of dry IDA sand sieved at 2 mm. The initial concentration of each metal in solution was 0.0125 mol/kg of water. Each suspension was filtered with 0.45 μm filters after a predetermined contact time varying between 15 minutes and 24 hours. The filtrates were acidified with $HNO_3$ and metals in solution were analysed by atomic absorption spectrometry (AAS). From mass balance calculations, the partition of metals in the solid phase was determined for each contact time.

Figure 1 shows the metal concentrations in the solid phase for the batch tests (Dubé 2001). For all four metals, it can be seen that there was a rapid partition of metals in the solid phase during the first hour of contact. This initial partition was greater for Pb (approximately 55 meq/kg) than for the other metals (between 30-35 meq/kg). For Cd and Zn, the concentration of metals in the solid phase began to decrease after 2 hours of contact. On the other hand, the lead concentration in the solid phase kept increasing after 2 hours of contact time and the copper concentration showed less variation for longer contact times.

For the same soil in contact with similar metal solutions, Lassabatère et al. (2007) showed, using scanning electron microscopy, that metal phases precipitate preferentially on carbonate grains and tend to form a coating around the grains. In their Phreeqc model, Lassabatère et al. (2007) combined equilibrium precipitation of metal carbonates and surface complexation to obtain a good fit to their experimental results. In the exploratory model proposed in this paper, it is hypothesized that the release of Cd and Zn observed in Fig. 1 could be due to a rapid initial precipitation of Zn and Cd carbonates as calcite surfaces and $CO_3^{2-}$ anions were available, and a subsequent dissolution of the same carbonate minerals as the solution $CO_3^{2-}$ activity decreased because of precipitation of less soluble lead carbonate and because of coating on the soil carbonate grains.

The metal elution tests were conducted in permeameters 10 cm long by 10 cm in diameter. IDA sand, sieved at 1 cm, was compacted in the permeameters. For the two selected elution tests, the soil columns were saturated with de-aired water after displacing the air in the pore volume using $CO_2$, a more soluble gas. The first step of the metal elution tests consisted in the elution of a conservative tracer, i.e. bromide, to characterize flow heterogeneity, i.e. the presence of a portion of the pore volume acting as preferential pathways. A KBr solution with an ionic strength equal to that of the metal solution used for the metal elution test that followed was prepared. At the beginning of each of the two tests, a tracer pulse equivalent to one pore volume was injected in the soil. A 2.5 cm pressure head was applied to the permeameters, which resulted in a hydraulic gradient of 1.25. During each tracer elution, the $Br^-$ concentration was measured in samples collected at the permeameter outlet by ion chromatography.

Figure 2 presents the results for two conservative tracer tests conducted on two duplicate soil columns identified as C1R+25 and C2R+25. For these duplicate tests, a positive pressure head of 2.5 cm of water was maintained in the soil. The soil was saturated and the mean porosity values were respectively 31.2 and 34.6 % for tests C1R+25 and C2R+25. The Darcy velocity values were respectively 0.214 and 0.311 cm/min. An advection-dispersion (AD) model (e.g., Fetter 1999) was fitted on the experimental data. Dispersivity values of respectively 3.5 and 3.9 cm were obtained. A mobile-immobile (MIM) flow model (van Genuchten and Wieranga 1976) was also fitted (not shown or used herein) which provided a dispersivity value of 0.9 cm. The latter were considered more representative of the largest heterogeneity in the soil column, namely the largest grain size of 1 cm. Nevertheless, for the purpose of the current study, dispersivities obtained using the AD model were used.

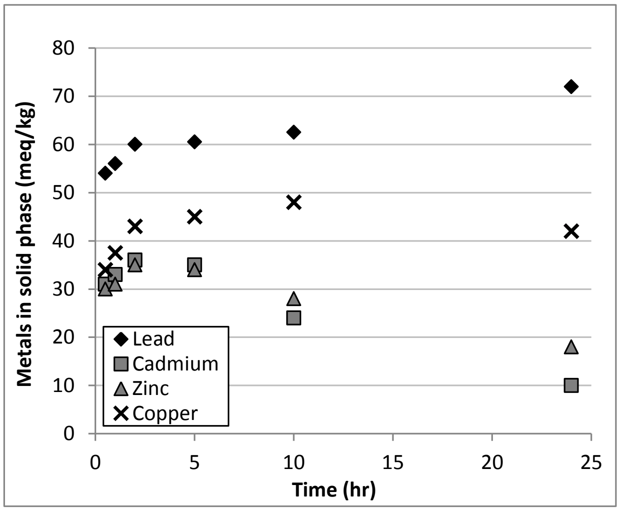

Figure 1. Metals in solid phase during batch tests (data from Dubé 2001).

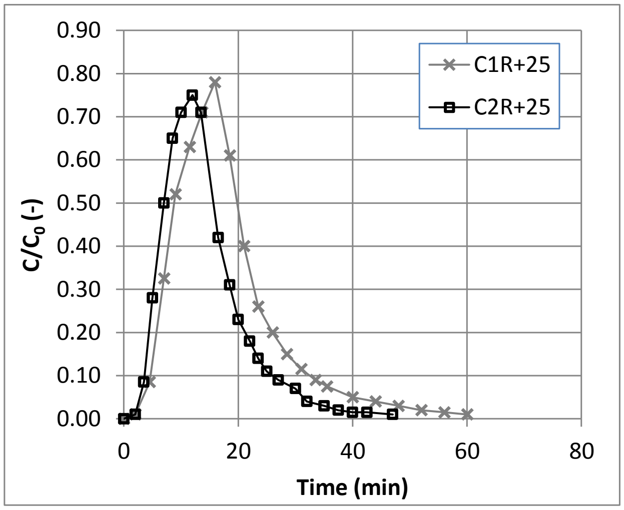

Figure 2. Experimental results for the conservative tracer tests (data from Dubé 2001).

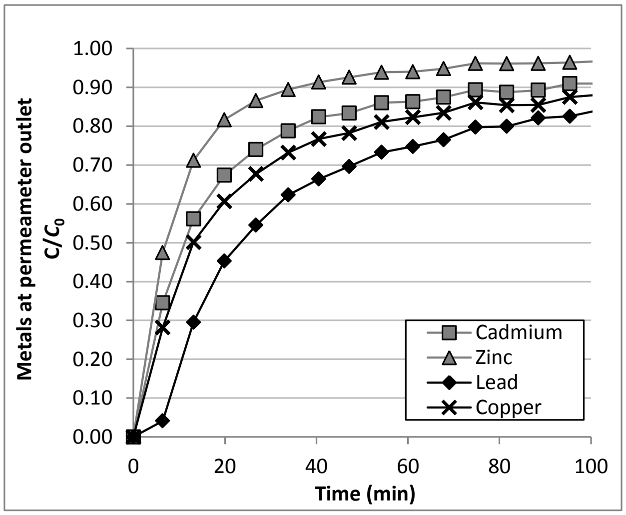

Figure 3. Experimental results for the metal elution test (data from Dubé 2001).

After the tracer elution tests, a solution of metal nitrates, identical to that used in the batch test, was continuously injected at the permeameter inlet from the start of the test. Samples were collected at the permeameter outlet and metals were filtered and analysed using AAS. After the test, the soil columns were extracted from the permeameters and sampled at different lengths to determine the concentration profile for metals in the soil.

Figure 3 shows the mean results for the two duplicate metal elution tests conducted with the same soil columns as those used for tracer elution. It can be seen that the four metals show different level of relative retardation in the following order of increasing retardation: zinc, cadmium, copper and lead. This pattern is coherent with the concentration of metals in the solid phase for the batch tests presented in Figure 1 after one hour of contact time. The metal concentrations in the solid phase of the soil columns after extraction were ordered the same way.

## 3 NUMERICAL MODELS

Figure 4 shows a schematic representation of the structure of an iCP project. Typically, at least five different input files are needed for a given project and one COMSOL output file is generated to store the simulation results. The main input file (input.icp) holds the name of the COMSOL and Phreeqc input files and the master time stepping scheme for the simulation. Selected results are stored in the output file for each of the master time steps. Shorter adaptive time steps are taken by the COMSOL and Phreeqc solvers during each of the master time steps.

The COMSOL input file (input.mph) contains an iCP interface for solute transport. Interfaces for any other physics or differential equations (e.g., heat transfer) can be added. The COMSOL input file also contains parameters for the solute transport equation. The COMSOL output file (output.mph) is created from the input file. A dummy physics is added by iCP in the COMSOL file to store the Phreeqc results.

Three input files are typically needed for Phreeqc: one for the initial conditions and kinetics law parameters (domain.pqi), a second file for the boundary condition (boundary.pqi) and a third file for the geochemical database (database.dat). Both domain.pqi and boundary.pqi are centered on SOLUTIONS blocks that define a chemical analysis for the solution. The domain.pqi file also includes a KINETICS block with parameters for the kinetics laws. As recommended in the iCP documentation, the RATES block that defines the rate laws based on lines of code programmed in Basic were moved to the database file.

The numerical modelling was performed in three steps. The first two steps allowed the parameters of the Phreeqc and COMSOL input files to be determined. During the third step iCP was used to model the metal elution test.

In the first step, the batch tests of Dubé (2001) were modelled with Phreeqc only to try reproducing the metal concentration in the solid phase after 24 hours (Fig. 1). To test the metal precipitation hypothesis introduced in section 2, a series of simple kinetics laws were assumed for the precipitation of metal carbonates (Appelo and Postma 2005):

$$R = k(1-\Omega)^n \text{ (for } \Omega \le 1) \qquad [1]$$

$$R = -k(\Omega-1)^n \text{ (for } \Omega > 1) \qquad [2]$$

where $R$ is the rate of dissolution or precipitation for the carbonate minerals (mole per unit of time, positive sign for dissolution), $\Omega$ is the saturation ratio, $n$ is an exponent and $k$ is a rate constant. Both $n$ and $k$ depend on the solution composition and must be fitted to experimental data. The rate constant $k$ is also proportional to total grain surface, or solid mass. The saturation ratio is calculated by Phreeqc (variable *SR*). It corresponds to the ratio between the ion activity product for the reactants of the precipitation reaction, and the equilibrium constant for the same reaction.

To simplify the model, only three metals were taken into account for precipitation: Pb, Cd and Zn. The metals were assumed to precipitate respectively as cerussite ($PbCO_3$), otavite ($CdCO_3$) and smithsonite ($ZnCO_3$). Figure 5 shows an example of KINETICS and RATES blocks used to program the kinetics laws for smithsonite. As mentioned previously, the KINETICS block is featured in the domain.pqi file while the RATES block is featured in the database.dat file.

The main carbonate mineral in the IDA sand was assumed to be calcite. For calcite dissolution, the default kinetics law in Phreeqc was used (Appelo and Postma 2005; Plummer et al. 1978). Two parameters are needed with this law. The first parameter ($A/V$) corresponds to the ratio between calcite surface area and water volume in $dm^{-1}$. Assuming spherical grains, this parameter depends on the grain diameter ($d$), the soil dry mass ($M_s$), the mass of water ($M_w$) and the calcite content in the soil ($P_{calcite}$):

$$A/V = \frac{6 P_{calcite} M_s}{G_s M_w d} \qquad [3]$$

where $G_s$ is the calcite specific gravity assumed to be 2.7 in this case. For the batch test, assuming a grain diameter of 0.04 mm, $A/V = 89\ dm^{-1}$. The second parameter allows the decrease in grain surface area with dissolution to be taken into account. A typical value of 0.67 was assumed for this parameter (e.g., Appelo and Postma 2005). This value is based on the assumption that the calcite grains remain spherical with dissolution.

For the simulations, the two parameters in Eqs. 1 and 2 were adjusted manually for each metal. The mass of water (0.01 kg), and the metal ($1.25\times10^{-2}$ mol/kg of water) and nitrate concentrations ($1\times10^{-1}$ mol/kg of water) used in the Phreeqc model corresponds to the experimental parameters. The initial number of calcite ($CaCO_3$) moles in 1 g of soil ($1.6\times10^{-3}$ mol) was based on the carbonate content ($P_{calcite}$ = 16 %) measured by Dubé (2001) for IDA sand. During the simulation, this initial number of moles was adjusted to take into account the limited availability of calcite because of the precipitation of a coating of metal phases around the calcite grains during the batch tests (Lassabatère et al. 2007). For each simulation, the solution pH was calculated from charge balance (option "charge" in the SOLUTIONS block) and the solution temperature was set at 20 °C, a realistic temperature for laboratory experiments.

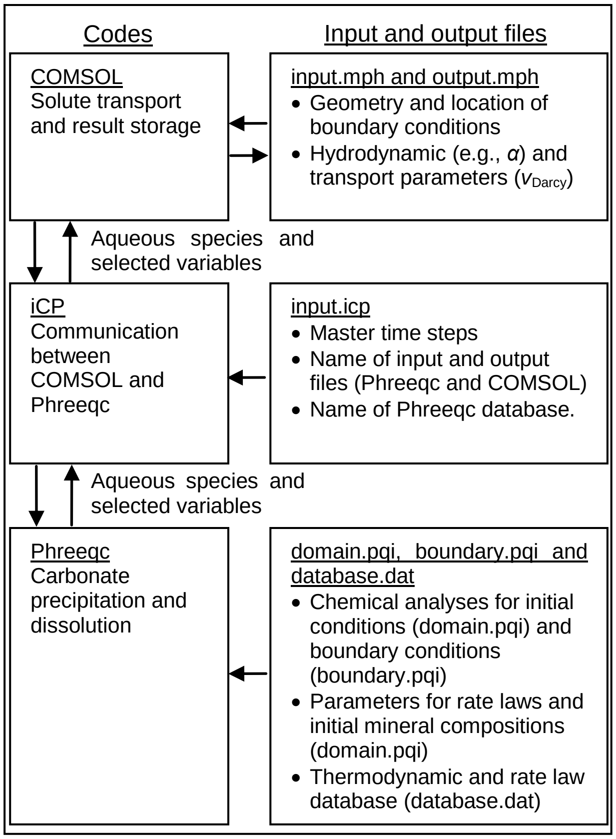

Figure 4. Schematic representation of the structure of an iCP project.

```
KINETICS
Smithsonite
   -m       0  #initial number of moles
   -m0      0  #initial number of moles
   -parms   2e-9  2  #correspond to PARM(1) and PARM(2)
   -tol     1e-10

RATES
Smithsonite
-start
  1 rem Appelo and Postma model with combined constants
  5 rem PARM(1) = k, PARM(2) = n
10 sr_c=SR("Smithsonite")
20 IF sr_c >1 THEN moles = -PARM(1)*(SR(“Smithsonite”)- \
     1)^PARM(2) * TIME ELSE moles = PARM(1)*(1- \
     SR("Smithsonite"))^PARM(2) * TIME
30 SAVE moles
-end
```

Figure 5. Examples of KINETICS and RATES blocks for the precipitation of smithsonite.

For the second modelling step, the tracer tests were modeled with COMSOL. The solute transport interface from the subsurface flow module was used. The following 1D mass conservation equation for the transport of chemical species in groundwater was used:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\alpha v_{Darcy}}{\theta}\frac{\partial C_i}{\partial x}\right) - \frac{v_{Darcy}}{\theta}\frac{\partial C_i}{\partial x} \quad [4]$$

where $\theta$ is the soil porosity, $C_i$ is the concentration of solute *i, x* is the depth coordinate in the permeameter*, $\alpha$* is the hydrodynamic dispersivity and $v_{darcy}$ is the Darcy velocity. The $\alpha$ values determined by Dubé (2001) were used to simulate test C1R+25 and C2R+25 (Fig. 2). The numerical results obtained with COMSOL were compared to those presented by Dubé (2001) for the same equation and the same dispersivity values to validate the results obtained with COMSOL.

In the third step, an iCP model was used to simulate the metal elution test. The iCP model combined the rate law parameters from step 1 with the hydrodynamic parameters from step 2. For the hydrodynamic part of the model, mean values of the hydrodynamic parameters for tests C1R+25 and C2R+25 were used ($\alpha$ = 0.037 m, $v_{Darcy}$ = 0.263 cm/min and $\theta$ = 32.9%). For Phreeqc, the *k* value for the precipitation rate law of each metal carbonate was multiplied by 5507 to take into account the mass of soil in contact with 1 kg of water, the default water mass in Phreeqc. For calcite, the number of moles was also adjusted to correspond to the number of moles in contact with 1 kg of water (0.468 mol). The *A*/*V* ratio for calcite was multiplied by 55.1 to take into account the higher soil/water ratio for the elution test. Finally, the SOLUTIONS block was modified to take into account the total number of moles of carbonate (C(4) in Phreeqc) and calcium in equilibrium with calcite ($1.187\times10^{-4}$ mol/kg of water). This change was based on the assumption that the pore water had sufficient time to equilibrate with calcite in the soil between the tracer test (step 2) and the metal elution test (step 3). This change was found to have an impact on the simulation results.

## 4 RESULTS AND DISCUSSION

Figure 6 shows a comparison of the experimental and numerical metal concentrations in the solid phase for the batch test conducted by Dubé (2001). Figure 6 shows that a model based on the precipitation and dissolution of metal carbonates can reproduce some features of the experimental curves, albeit not perfectly. For instance, by assuming slower precipitation for lead carbonate (cerrusite), and faster precipitation for zinc carbonate (smithsonite), the Phreeqc model can replicate the Zn release from the solid phase that begins 4 hours after the test beginning. On the other end, this trend cannot be replicated for cadmium carbonate (otavite). In fact, at the end of the batch test, the solution is still saturated with respect to otavite ($\Omega$ value is still close to 100). Figure 6 also shows that slowing down the precipitation of cerussite and otavite does not allow reproducing the rapid increase in metal concentration in the solid phase at the beginning of the test. When Eqs. 1 and 2 are used, it appears impossible to replicate both the rapid partition in the solid phase at the beginning of the experiment and the long term trend for the second part of the test (from *t* = 2 hours to *t* = 24 hours).

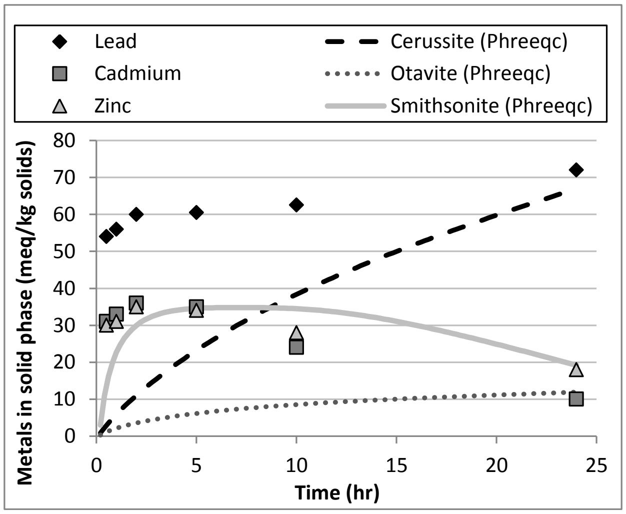

Figure 6. Comparison of experimental and numerical results for the batch tests.

The *k* and *n* values that best replicated the metal concentrations in the solid phase at the end of the 24 hour batch test were chosen. Table 1 gives the parameter values for each metal carbonate. To obtain the results presented in Fig. 6, the moles of calcite in 1 g of soil had to be decreased from $1.6\times10^{-3}$ mol according to the carbonate content given by Dubé (2001) to $0.85\times10^{-4}$ mol. This does not appear unrealistic as it reproduces the impact of the coating of metal phases that was observed by Lassabatère et al. (2007) around calcite grains in a similar experiment. In effect, the precipitation of metal phases around the calcite grains isolates the calcite grains from the solution, thus slowing down its dissolution, the production of carbonate ions and metal precipitation.

Table 1. Selected set of parameters for the kinetics laws (step 1, batch test model with Phreeqc).

| Mineral | Parameter | |
|---|---|---|
| | k (mol/s) | n (-) |
| Otavite | $3\times10^{-15}$ | 2 |
| Smithsonite | $2\times10^{-9}$ | 2 |
| Cerussite | $4.2\times10^{-13}$ | 1 |

Two approaches are suggested to obtain a better fit between the experimental and numerical results presented on Fig. 6. First, a more refined set of rate laws could be used for precipitation and dissolution of metal phases. The rate law used for calcite dissolution in this paper is a good example (Plummer et al. 1978). With this rate law, the rate of dissolution does not simply depend on the ion activity product for $Ca^{2+}$ and $CO_3^{2-}$. It also depends on the solution pH. With the second approach, both surface complexation and precipitation/dissolution phenomena could be considered. In Phreeqc, this would imply using both RATES and SURFACE blocks. In this case, surface complexation could explain the rapid partition of metals in the solid phase while precipitation/dissolution would explain the trend in the second part of the test, from *t* = 2 hours to *t* = 24 hours. It must be remembered that surface complexation was successfully used in the Phreeqc script of Lassabatère et al. (2007) to model similar experiments.

Validating the mineralogy of the metal phases would also improve the model. With scanning electron microscopy, Lassabatère et al. (2007) confirmed the precipitation of lead carbonates in a similar experiment. The mineral phases associated with cadmium and zinc were less clear. It was observed that zinc and cadmium were associated with the same phase and that they tended to precipitate inside porous carbonate grains. For the numerical model presented in this paper, otavite and smithsonite were selected as the cadmium and zinc phases simply because of their availability in the standard Phreeqc database.

Figure 7 compares the numerical and experimental breakthrough curves for the tracer tests. The bromide concentration at the outlet is normalized by its concentration in the slug at the inlet. The breakthrough curves obtained with COMSOL in this study are nearly identical to the one obtained by Dubé (2001) using a Mathcad application based on the same equation and using the same parameters. The difference between the two experimental breakthrough curves is mainly caused by the difference in hydraulic conductivity between the two specimens (0.214 cm/min for C1R+25 and 0.311 cm/min for C2R+25). Interestingly, the percentage difference between the hydraulic conductivity for the duplicate tests (37 %) is larger than the percentage difference for the best-fit dispersivity values (10 %). The same observation can be made from the other duplicate tracer tests performed on saturated sand by Dubé (2001) (pressure head equal to 0 cm, not shown here). This seems to imply that dispersivity is less variable than hydraulic conductivity for homogeneous materials. Globally, the hydrodynamic aspect of the model is much easier to replicate than its geochemical aspect.

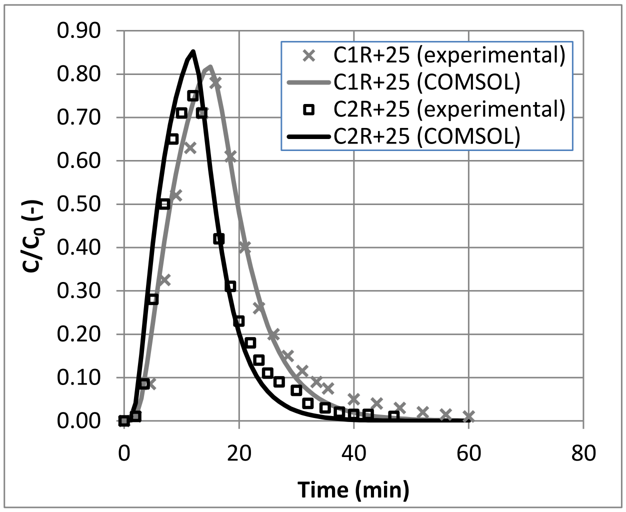

Figure 7. Comparison of experimental and COMSOL results for the tracer tests.

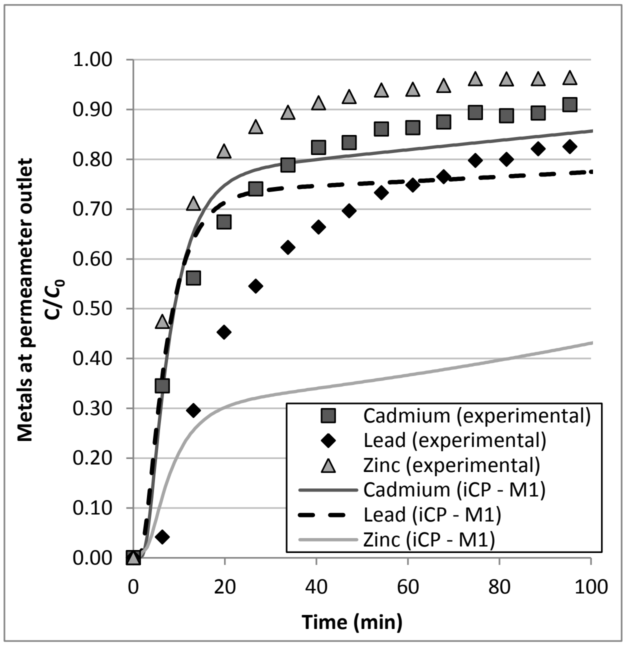

Figure 8. Comparison of experimental and numerical results for the metal elution test (Model M1).

Figures 8 and 9 show the numerical and experimental breakthrough curves for the metal elution tests. Results for two versions of the numerical model are shown. Model M1 (Figure 8) corresponds to the model introduced in the previous section. The *k* values for the rate laws obtained through the batch test were multiplied by 5507 to take into account the different soil mass for the batch and elution tests. In this case, the elution order for Zn and Pb is reversed compared to the experimental results. The numerical breakthrough curve for lead also has a different shape than the experimental curve, the latter being more rounded. For cadmium, the fit on the experimental results is relatively good. For zinc, the numerical concentration at the outlet is much lower than for the experimental results.

With Model M2 (Fig. 9), the *k* values were changed to obtain a better fit on experimental results. For cerussite, otavite and smithsonite, the *k* values were respectively divided by 2, 8 and 600. This allowed the lower metal concentrations at the outlet for *t* values greater than 60 minutes to be replicated, but not the general shape of the breakthrough curves. The experimental breakthrough cures are more rounded than the numerical curves. Globally it can be seen that the rate laws determined from the batch test by trying to replicate the metal concentration in the solid phase after 24 hours cannot be applied to the metal elution tests. This could be related to the markedly different scales of contact time for the batch test and metal elution test. The batch test has a total duration of 24 hours while the mean contact time during the metal elution test is on the order of 10 minutes based on the conservative tracer velocity. It should be noted that the numerical curves on Fig. 6 failed to replicate the concentration in the solid phase at the beginning of the batch test (*t* < 1 hour).

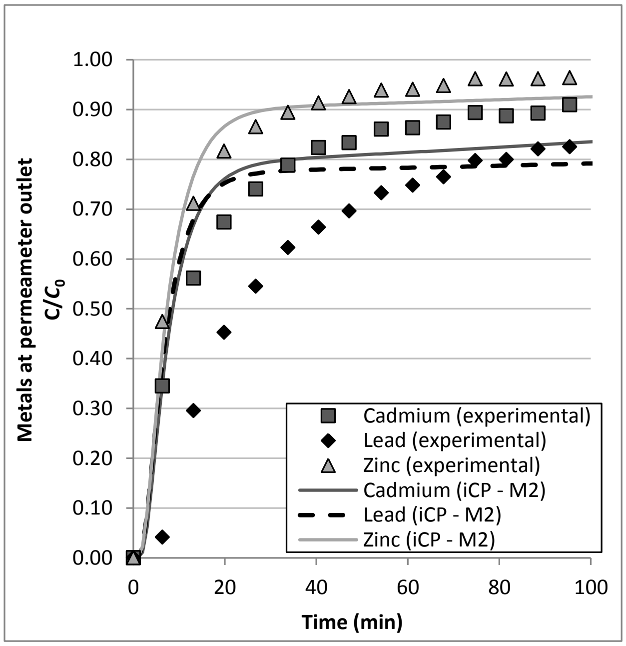

Figure 9. Comparison of experimental and numerical results for the metal elution test (Model M2).

An interesting result from the numerical model is that metal carbonates tend to precipitate near the permeameter outlet as the pore water contains less carbonate near the inlet. As it flows through the permeameter, the pore water equilibrates with calcite to some extent and the $CO_3^{2-}$ concentration increases. The same observation was made by Dubé (2001) when he sampled the soil at different depths in the permeameter at the end of the metal elution tests. However, the higher metal concentration at the base of the permeameter was less striking than with the numerical model.

## 5 CONCLUSION

The iCP interface between Phreeqc and COMSOL was used to model two laboratory experiments conducted by Dubé (2001). The first experiment was a batch test where Cd, Cu, Pb and Zn nitrates were put in contact with a calcareous soil (IDA sand). The second was an elution experiment using soils columns in permeameters. The elution test consisted in the elution of a conservative tracer, followed by the elution of a solution of metal nitrates on the same specimens. The metal elution test combined the hydrodynamic aspect of the tracer test with the reactive aspect of the batch test.

The iCP model reproduced some of the features of the experimental results, but not all of them. The hydrodynamic part of the numerical model could easily replicate the experimental results for the tracer test (Fig. 7). It was found more difficult to simulate the geochemical aspect of the batch and metal elution tests (Figs. 6, 8 and 9). The simple rate laws that were assumed for the precipitation of Cd, Zn and Pb carbonates could not replicate the partition of metals in the solid phase that was observed for the different scales of contact time for batch and elution tests (10 minutes for elution tests and 24 hours for batch tests).

Several approaches have been proposed to obtain a better fit between the experimental and numerical results. Among others, it is proposed to combine in the Phreeqc input file a SURFACE block to model sorption and the initial uptake of metal in the solid phase with RATES and KINETICS blocks for the precipitation and dissolution reactions. The geochemical model would also benefit from a better characterization of the Cd, Pb and Zn mineral phases, and of the mechanisms controlling metal partition in the solid phase at the beginning and near the end of the batch test.

Even if the model does not reproduce perfectly the experimental results, this paper highlights the usefulness of iCP as a tool to validate geochemical models. Devising a numerical model early in a research project allows experimental parameters to be optimized (e.g., batch test duration, hydraulic gradient or permeameter length for elution tests). When the first experimental results are in, this preliminary model can be updated. The discrepancy between the experimental and numerical results can then help refine the methodology and identify specific observation that would benefit our understanding of the mechanisms at work.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the funding of NSERC for this project. This research project was conducted as part of the first author Discovery Grant on multiphysics modelling and Champlain clays (RGPIN 2015-06728).

## REFERENCES

Appelo, C.A.J., and Postma, D. 2005. *Geochemistry, groundwater and pollution*. CRC Press, Boca Raton, FL, USA

Bélisle, M. 2013. *Influence de l'injection d'un traceur sur les courbes de restitution en écoulement naturel*. M.Sc.A. thesis, École Polytechnique de Montréal, QC.

Charlton, S.R., and Parkhurst, D.L. 2011. Modules based on the geochemical model PHREEQC for use in scripting and programming languages. *Computer & Geosciences* 37: 1653-1663.

Dubé, J.-S. 2001. *Modifications hydrodynamiques du comportement des métaux lourds dans un sol hétérogène présentant une contamination résiduelle en NAPL*. Ph.D. thesis, Université Laval, QC.

Duhaime, F., and Chapuis, R.P. 2014. A coupled analysis of cavity and pore volume changes for pulse tests conducted in soft clay deposits. *International Journal for Numerical and Analytical Methods in Geomechanics* 38(9): 903-924.

Fetter, C.W. 1999. *Contaminant hydrogeology*. Waveland Press, Long Grove, IL, USA.

Finsterle, S., Sonnenthal, E.L., and Spycher, N. 2014. Advances in subsurface modeling using the TOUGH suite of simulators. *Computers & Geosciences* 65: 2-12.

Lassabatère, L., Spadini, L., Delolme, C., Février, L., Galvez Cloutier, R., and Winiarski, T. 2007. Concomitant Zn-Cd and Pb retention in a carbonated fluvio-glacial deposit under both static and dynamic conditions. *Chemosphere* 69: 1499-1508.

Nardi, A., Idiart, A., Trinchero, P., de Vries, L.M., and Molinero, J. 2014. Interface COMSOL-PHREEQC (iCP), an efficient numerical framework for the solution of coupled multiphysics and geochemistry. *Computer & Geosciences* 69: 10-21.

Plassard, F., Winiarski, T., and Petit-Ramel, M. 2000. Retention and distribution of three heavy metals in a carbonated soil: comparison between batch and unsaturated column studies. *Journal of Contaminant Hydrolog*y 42: 99-111.

Plummer, L.N., Wigley, T.M.L., and Parkhurst, D.L. 1978. The kinetics of calcite dissolution in $CO_2$-water systems at 5 degrees to 60 degrees C and 0.0 to 1.0 atm $CO_2$, *American Journal of Science* 278:179-216.

Réginensi, F. 2009. *Évolution géochimique de l'eau interstitielle d'une argile de la mer Champlain*. M.Sc.A. thesis. École Polytechnique de Montréal, QC.

van Genuchten, M.T., Wieranga, P.J., 1976. Mass transfer studies in sorbing porous media I. Analytical solutions. *Soil Science Society of America Journal* 40:473–480.