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Present state and future directions of modeling of geochemistry in hydrogeological systems

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Abstract

A first step towards understanding and controlling the fate and dissemination of radioactive waste is to create a concise and comprehensive theoretical framework for the rather non-linear processes involved —hence the need for geochemical models. Two classes of geochemical models are commonly used, i.e., static and hydrodynamic models. In contrast to static models, hydrodynamic models combine geochemical reactions with hydrogeological processes such as ground-water flow, diffusion and dispersion. In this review, we examine the present state of geochemical models in terms of included processes, thermodynamic databases, missing phenomena, numerical behavior and performance. It is shown that over the past decade, significant progress has been made with respect to modeling of geochemistry in hydrodynamic systems: this is illustrated by describing several applications. Finally, we focus on the perspectives of geochemical modeling in the assessment of the safety of nuclear waste disposal.

Keywords: reactive transport, modeling, geochemistry, review

1 Introduction

Performance assessment studies for radioactive waste repositories often rely on long-term predictive modeling of radionuclide migration through the near- and far field

barriers. Two aspects must be covered by the model: geochemical and hydrodynamic processes. Geochemical processes include, among others, aqueous speciation and redox reactions, interface reactions, precipitation/dissolution of minerals and colloids. Hydrodynamic processes include mainly diffusion and migration due to advective forces, leading to dispersion of the chemical species in space and time. Traditionally, geochemical and hydrodynamic processes are modeled as independent systems. This is understandable in view of the mathematical concepts, i.e. (simplifying) an algebraic system on the one hand and a partial differential system on the other. Moreover, geochemistry and hydrology have often been considered as distinct scientific disciplines, practiced by, respectively, chemists and hydrologists.

However, geochemical and hydrodynamic processes are closely entangled. For example, the aqueous background chemistry varies over time and space as a function of the kinetically controlled reactions with the minerals composing the rock matrix (and depends notably on pH, Eh and inorganic carbon concentration) and therefore depends on the hydrodynamic regime. Porosity and permeability may also change when minerals precipitate or dissolve, or when colloids or polymeric structures mask pore-throats.

We therefore need a coupled approach, assessing the effect of combined and simultaneously occurring geochemical and hydrodynamic processes. Reactive transport models are developed for this purpose. They are tools which help to understand the system as a whole, and to quantify the fate of e.g., radionuclides along a reaction path as a function of multiple, interdependent reactions. This review resumes the current state of geochemical models and reactive transport models in terms of processes, fundamental principles and examples.

2 Modeling of geochemical processes

Aqueous reactions

One of the fundamental tasks of a geochemical model is to calculate the spectrum of species in the aqueous phase since the concentrations of the individual species depend on the solution characteristics (e.g., pH, Eh, alkalinity, ionic strength). Most of the currently known geochemical models use the assumption of local thermodynamic equilibrium (Westall et al. 1986; Wolery 1992; Bethke 1994; van der Lee 1998). Indeed, the bulk chemistry of most natural water is dominated by fast reactions which are at equilibrium at pertinent time-scales.

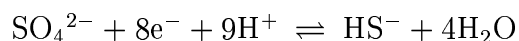
However, specific reactions (redox reactions, interface reactions, precipitation and dissolution) are kinetically controlled and some recent models express all reactions in terms of first- or second-order kinetic formulations (Soetaert et al. 1996). A fully

kinetic approach also makes it possible to simulate equilibrium reactions under the assumption that, at equilibrium, the net reaction rate is zero. This is known as the *principle of detailed balancing* (or *microscopic reversibility*) (Lasaga 1984; Morel and Hering 1993). Another approach to introducing kinetically controlled reactions in an aquatic system is to mix kinetic and equilibrium reaction laws. The idea is attractive because one can recycle existing models and solution methods developed for the thermodynamic equilibrium approach. However, kinetic laws fit awkwardly into the framework of general algebraic solvers. Despite the increased complexity of the numerical solution of a mixed kinetic-equilibrium approach, several models use this approach (Bethke 1996; van der Lee 1998). Properly implemented, the mixed approach is faster than that of full kinetics for systems that are dominated by equilibrium reactions. Last but not least, extended, relatively stable and consistent databases are available for equilibrium chemistry, while kinetic databases are still small, evolving and, by definition, much more dependent on the chemical conditions.

Redox reactions

Near-field performance assessment studies require a precise understanding of the local redox conditions, since they define the solubilities of many radionuclides. In most natural systems, the aqueous fraction Fe(II)/Fe(III) *controls* the redox potential (Grenthe et al. 1992). Since ferric iron is relatively insoluble, reduction of Fe(III) generally involves two steps: dissolution of the solid (e.g., Fe(OH)₃) and reduction of Fe(III) species. Both steps are subject to kinetics, but the rate-limiting step depends on the solution chemistry. Microbial mediation is often mentioned as one of the kinetic rate-determining factors (van Cappellen and Gaillard 1996).

Redox reactions are of major importance for solubility and mobility of waste material and most geochemical models include this process. Reactions involving the transfer of more than one electron and major rearrangement between reduced and oxidized forms of a redox couple are in general slow, e.g.,



Nevertheless, only the *equilibrium* approach is commonly available in geochemical models. Fortunately, the equilibrium approach can be adapted to case-specific studies assuming partial redox disequilibrium (McNab and Narasimhan 1994; Bethke 1996; Keating and Bahr 1998).

Dissolution/precipitation of minerals and colloids

Dissolution and precipitation reactions are extremely important processes in most natural systems because they control the fluid chemistry, especially in terms of buffer-

ing the pH and redox potential. Therefore, all recent models include these processes (Bethke 1994; Parkhurst 1995; van der Lee 1998). Precipitation occurs as soon as the solution becomes *oversaturated* with respect to a solid phase. Activity corrections are essential when the degree of saturation with respect to a solid is calculated. Correction for non-ideality (activity) is generally based on simple models (Davies, Debye-Huckel or B-Dot) but for more concentrated solutions, specific ion interaction theories must be used, e.g., SIT, Pitzer or Bromley equations (Grenthe et al. 1997). In an equilibrium model, supersaturation of the mineral is generally not allowed and, potentially, precipitation occurs as soon as the saturation index exceeds zero. Whether or not the mineral actually precipitates is, however, a matter of kinetic control of the reaction. It appears that a true equilibrium approach is not appropriate for commonly considered time- and space-scales (Appelo and Postma 1993; Sposito 1994).

Interface processes

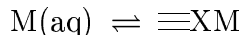
Interface processes are reactions with solid phases and lead, under dynamic conditions and if the solid phase forms part of the rock, to retention of aqueous species. We distinguish six different reaction models, which are expressed in terms of mol-balance equations in Table 1. The list is not exhaustive but it summarizes the most important reaction mechanisms such a way that they can be compared.

With virtually no exception, mineral and colloidal surfaces in nature have a capacity to react with protons. A metal can exchange with one or more protons or metals at these functional groups. Surface complexation reactions can alter the solution composition when protons are taken up or released. Furthermore, a ligand or anion can be exchanged at functional groups with positive charge (Dzombak and Morel 1990).

Ion exchange is an important interaction mechanism for metals in clays (Sposito and LeVesque 1985; Charlet 1993; Appelo and Postma 1993; Wang et al. 1997). Table 1 schematically illustrates some different ion exchange reactions. Translation of the the second cation exchange equation of Table 1 into a mass-action law expression is not straightforward and different conventions are proposed (see e.g., Appelo and Postma (1993)).

Surface precipitation (or *co-precipitation*, *solid-solution formation*) is somewhat different from the previous reactions. In principle, solid solutions are the result of the (slow) *aging* of a surface after a (fast) surface complexation reaction. In certain circumstances, however, the structural re-organization of the surface is fast at the time scale of interest and the surface-complexation step is ignored (Tiffreau et al. 1995; Bruno et al. 1995).

The K_D approach should be mentioned as well, since it is still quite often used in modeling studies. By convention, the K_D is a coefficient which defines the distribution of the aqueous and adsorbed fractions of the sorbing species:



The K_D approach does not belong to the family of deterministic, thermodynamic models. However, the approach is useful if no further information is available, or as a initial modeling attempt. Some models include the K_D approach (van der Lee 1998), but due to the ad-hoc and condition-specific nature of the values, no generally applicable database with K_D values is available. Non-linear isotherms, e.g., Langmuir and Freundlich isotherms, should be considered as *refinements* of the K_D approach.

Most models include one or several of the surface-reactions listed here. Surface complexation is currently the most popular interface model. Electrostatic corrections are generally included and implemented using double-layer models (Dzombak and Morel 1990), triple-layer models (Righetto et al. 1995) or constant-capacitance models.

3 Modeling transport of reactive solutions

Reactive transport modeling has two facets: modeling of hydrodynamic processes leading to migration and dispersion of chemical species (transport) and geochemical processes (reactivity). Both facets are present simultaneously and continuously, and they are interdependent. Geochemical reactions depend on residence time and the hydrodynamic properties of the medium may change as minerals precipitate or dissolve and as colloids clog pores, which leads to permeability changes. Table 2 shows a brief summary of models, together with their geochemical and transport 'engines'. The table is not exhaustive: many unnamed codes have been developed and published.

In order to illustrate the methodology, we introduce, as in Yeh and Tripathi (1989), a specific-purpose transport operator \mathcal{L} . Accordingly, transport of an aqueous, colloidal or gaseous species (C_j) is expressed by the following equation (e.g., Cederberg et al. (1985)):

$$\frac{\partial(\omega C_j)}{\partial t} = \mathcal{L}(c_j) \quad (1)$$

where ω denotes the porosity of the medium, c_j the *mobile* concentration of the species and C_j is the total concentration such that $C_j = c_j + \bar{c}_j$, \bar{c} is the immobile concentration. For a multi-dimensional transport system including advection, diffusion and dispersion, the transport operator yields:

$$\mathcal{L}(c_j) = \nabla \cdot (\omega D_j \nabla c_j - \omega u c_j) \quad (2)$$

where D_j includes diffusion and dispersion which can be species-specific (see e.g., Bear (1972), de Marsily (1986)) and u is the advective flow velocity. Note that the porosity is explicitly included in the equations: indeed, the porosity is subject to change in time and space due to geochemical processes such as precipitation, dissolution or clogging of pores by colloidal retention.

A second specific-purpose operator, the reaction operator \mathcal{R} , integrates the entire geochemical model and is used to provide a precise estimate of vector \mathbf{c} :

$$\mathbf{c} = \mathcal{R}(\mathbf{C}) \quad (3)$$

An explicit description of \mathcal{R} , similar to e.g., equation (2) for the transport operator \mathcal{L} , is unavailable since \mathcal{R} includes all the processes described in section 2 of this review. Currently, most reactive transport models link geochemistry (\mathcal{R}) and transport (\mathcal{L}) with one of the following approaches:

- *Sequential iterative approach*
- *Sequential non-iterative approach*
- *Global implicit approach*

One of the conclusions of the often quoted review paper by Yeh and Tripathi (1989) states: “Only those models that employ the sequential iterative approach can be used for realistic applications”. This statement is outdated: several recent studies have successfully applied other approaches (Steeffel and Lasaga 1994; van Cappellen and Wang 1996; van der Lee 1997c). Nevertheless, the fact is that many reactive transport models formerly or currently in use use the sequential iterative approach. A major advantage is that a stand-alone, fully featured geochemical code can be used as the reaction-engine, thus facilitating development, testing and maintenance.

In the sequential approach, transport and chemistry are solved one after the other within a single time step. As follows from equations (1) and (3), the steps are dependent on each other: the transport step depends on variables c_j which are known only after evaluation of the reaction step and therefore uses an *estimate* of c_j , leading to an approximate solution. The error depends on many factors, such as the time step and the geochemical reactivity of the medium. Iterative improvement of the solution is required to reduce the error to an acceptable level. Figure 1 illustrates the iteration method applied to each time step.

The combined transport and geochemical model leads to complex numerical behavior and the iterative procedure may fail to converge. For this reason, some models suppress the iterative improvement of the solution, which leads to the so-called Sequential Non-Iterative Approach (Vinsot and Coudrain-Ribstein 1989; Pfingsten 1994; Schäfer

et al. 1998; Yabusaki et al. 1998). It is general assumed that sufficiently small time steps will reduce the error to an acceptably low value. The study by Yeh and Tripathi (1991), however, clearly demonstrates that iterative improvement is of critical importance for the accuracy of the model.

The global implicit (or *one-step*) approach seeks to explicitly integrate the reaction equations into the transport equation and then solve the fully coupled algebraic-partial differential problem. The reactive step forms an *implicit* part of the global transport problem. Several reactive transport models have been developed by this approach (Miller and Benson 1983; Steefel and Lasaga 1994), sometimes including Monod kinetics for organic-matter degradation pathways (van Cappellen and Wang 1996). In theory, the approach can solve geochemically complex systems but in practice, this leads to very complex mathematics and excessive memory requirements even for moderate systems (Steefel and MacQuarrie 1996). However, the approach may lead to better global convergence for large time steps.

4 Applications

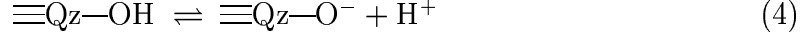
The combined effects of hydrodynamic and geochemical processes often produce unexpected results. Indeed, although individual processes may be simple (e.g., mass-law equations, the transport equation, etc.), the fully coupled approach deals with a complex ensemble of simultaneously occurring reactions with sometimes unforeseen behavior. Quantification of the overall impact of individual but interdependent processes represents one of the principle strengths of reactive transport models. In order to illustrate this point and related issues, we consider the examples given below. All simulations were carried out with the HYTEC code which uses CHESS for its geochemical calculations¹.

Migration of toxic metals through sand

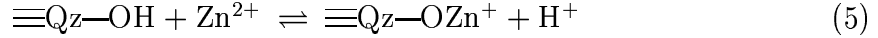
In order to study the migration of toxic metals in soils, column experiments were carried out with tracers and zinc (Warwick et al. 1998). The column material consists of unconsolidated sand (BDH Laboratory Supplies, GPR grade), purchased already purified by acid and with a specified particle size of between 0.1 and 0.3 mm i.e. 50 – 150 mesh. The hydrodynamic properties (porosity, dispersivity) were determined by a step-input experiment by injecting 0.5 ml of tritiated water. A constant-feed technique was used for the zinc migration experiments, with a 0.5 molar NaCl solution at a pH of 6.1. At this pH, most aqueous Zn-complexes and precipitation can be

¹CHESS is available via Internet: <http://chess.ensmp.fr>

disregarded. Pure quartz (Qz) is negatively charged over the entire pH range of interest ($\text{pH} > 2$), protonation reactions are therefore negligible. Deprotonation is expressed by:



The $\log(K)$ for BDH quartz grains has been determined (van der Lee 1997b) and yields ~ -7 , close to values commonly found for quartz and amorphous silica (Bolt and Riemsdijk 1987; Rea and Parks 1990). The total site density was determined as being $34.4 \mu\text{eq}$ per liter of pore water for a porosity of 0.3 and a total, volumetric surface area of $8.6 \text{ m}^2/\text{l}$. The surface complexation reaction (see Table 1) with species Zn^{2+} is written as follows:



Other, heterovalent surface complexation reactions were not considered in this study. A $\log(K)$ of 0.5 was obtained for equation (5) by fitting experimental data from Warwick et al. (1998). This value includes a correction for electrostatic effects, based on the double-layer theory.

As the quartz surface complexes Zn^{2+} , protons are released which results in a decrease of pH. The H^+ front is moving considerably faster than the zinc, but more slowly than that of an ideal tracer. Also, the retention process tends to sharpen the front. This is clearly illustrated by Figure 2 that shows the fronts at different times.

The shape of the zinc front differs from the front of a *retarded* tracer: the curve is asymmetric, with a tailing that tends to increase with time. The tailing is the result mainly of the electrostatic effect, which leads to a *smearing* of the front. Moreover, protons are released as zinc is adsorbed, which modifies the equilibrium of the surface at the front. Tailing effects are often attributed to adsorption kinetics (Brusseau 1992) or to diffusion in specific parts of the medium (Bouchard et al. 1988). Here, it is shown that surface complexation and electrostatic interaction explain, at least part of, the tailing effects.

This example demonstrates that, even for simple systems, migration of reactive chemicals requires a fully coupled approach. If not, conclusions can be wrong and extrapolations to other space- and time scales may be erroneous.

Modeling of long-term behavior of near field barriers

To model the efficiency of near-field barriers representing an important step in the assessment of the overall performance of a nuclear-waste repository. The geometric configuration and geochemical composition of near-field barriers are well characterized

compared to the geosphere. Moreover, the spatial scales at which the processes are studied are smaller (several meters). Nevertheless, barriers are of different chemical and mineralogical nature, leading to mixing of very diverse solutions. The following examples show how reactive transport models may contribute to the understanding of the overall behavior of near-field barriers over relatively long time scales, i.e. 1,000 to 10,000 years.

Migration and interactions in near-field barriers

Consider a near-field barrier composed of FoCa (a swelling clay, proposed as back-fill material in France) in contact with the surrounding host-rock, a clay-rock. FoCa is well characterized in terms of its composition and ion-exchange mechanism (Cranga et al. 1998). In the absence of reliable data of the clay-rock proposed by the French Waste Disposable Agency (ANDRA) as the host formation of a repository, data from the unperturbed part of the Tournemire clay formation, a well-characterized clay-rock (de Windt et al. 1999), were used. Table 3 summarizes the composition and main properties of both the clay-rock and the FoCa barrier.

We considered 25 cm of FoCa and 4.80 cm of homogeneous clay-rock. At the beginning of the simulation, the solutions start to mix due to diffusion (advection is expected to be negligible in these media). Given the composition of both solutions, aqueous Ca species diffuse in the clay-rock and aqueous Na enters the FoCa barrier, inducing cation exchange in both systems. Oxygen migrates from the barrier into the clay-rock, which leads to dissolution of pyrite and precipitation of ferrihydrite. The amount of sorbed Ca increases in the clay-rock, releasing mainly Na. The opposite reaction occurs in the FoCa barrier. As a consequence, there are precipitation and dissolution reactions in both formations.

Although described as a sequence, all reactions are tightly interwoven and interdependent. One way to illustrate the complexity of the system is to follow the evolution of a key parameter, such as the pH. Figure 3 resumes the most important reactions and shows the pH as a function of time and space in both formations. Note that the word 'fronts' is not adequate for this kind of system: we prefer to call them waves. The pH waves reflect, in the first place, precipitation and dissolution reactions. Inside the clay-rock, calcite and fluorite first dissolve, then precipitate further away from the FoCa barrier.

This simulation has many interesting features, such as precipitation-induced dissolution fronts, redox reactions and many more. Although it is too complex to outline here (an article, dedicated to this and related simulations is in preparation), a few important conclusions can be drawn and are shown in Figure 3. First, the stationary state is not reached, even after 1,000 years. Second, the boundary conditions (i.e.,

between the FoCa barrier and the clay-rock) vary in time. Consequently, it would be inaccurate to model the clay-rock with only a constant boundary condition representing the FoCa barrier (or *vice versa*) would be inaccurate. Modeling of a near-field system requires an integrated approach, that considers the heterogeneous system as a whole.

Expected porosity changes at the cement-clay interface

Experimental work by Lagneau and co-workers (CEA, France) is in progress in order to study the impact of geochemical transformations on the local porosity of a clay barrier (MX80) in contact with cement. Scoping calculations have been carried out with HYTEC for scales larger than the laboratory experiments (see Figure 4). The mineralogical compositions of the two zones, given in Table 4, lead to a pH of ~ 12.5 in the concrete, and ~ 7.9 in the clay.

The one-dimensional simulation illustrates the impact of phase transformations at the interface, particularly in the clay. Kaolinite and sodium-montmorillonite are thermodynamically unstable and dissolve to form K-feldspar, quartz, CSH(1.1), scolecite and talc, albeit according to slow reactions. The mineral phase transformation slowly migrates in the clay according to a specific pattern, depending on the relative stability of the minerals. This process alters the local porosity and, consequently, the permeability of the clay close to the interface. Figure 4 shows the expected porosity distribution at different times, calculated with the volumetric densities of the minerals.

This simulation was carried out with a relatively simple model, assuming full thermodynamic equilibrium (no precipitation- and dissolution-kinetics), disregarding redox reactions and without feedback of the geochemistry on the hydrodynamic parameters. In spite of the simplifying assumptions, the simulation is useful for understanding the major processes at the interface of two different media, for analyzing the experimental results and for designing laboratory experiments.

5 Discussion

Over the past decade or so, considerable progress has been made in the modeling of hydro-geochemical systems, particularly in the field of reactive transport. Until the early 1990s, reactive transport models included few processes, generally introduced for a specific study. Discrepancies between the simulation results and experimental data could safely be explained by neglected processes. Furthermore, limiting computing facilities forced researchers to reduce the number of species and reactions considered in their calculations.

Models available today can manage many geochemical processes, notably precipitation/dissolution, redox reactions, surface complexation, cation exchange, co-precipitation, kinetic reactions and, sometimes, colloidal reactions. These models are linked to extended databases, hence several hundreds of simultaneously reacting species can be considered. Nevertheless, a number of shortcomings in the coupled, reactive transport models should be mentioned.

First, a lack of conceptual understanding and data limits their use on natural systems. For example, co-precipitation reactions and the thermodynamic behavior of solid solutions in general are often studied, but a wide variety of modeling approaches seem to reflect the complexity of the process and, to some extent, a lack of conceptual understanding. Co-precipitation and surface complexation are closely related processes but none of the geochemical models, evaluated so far, includes these processes in a concise manner, i.e. formation of *new*, heterogeneous minerals *on the fly* of a simulation.

Limitations of the thermodynamic approach are often related to the formation of solids (precipitation of minerals, oxides and colloids, polymerisation of organic matter), due to unknown kinetic or equilibrium constants (Berner 1998), or lack of conceptual knowledge.

Most published reactive-transport modeling studies are based on the assumption of a homogeneous porous medium. Natural media are, as a general rule, heterogeneous both from a geochemical and a hydrogeological point of view. As stated by Lichtner (1996), the predictive capability of groundwater transport models is hampered by our inability to know the precise nature of porous media found in natural systems. Since geochemical and hydrogeological heterogeneities are related, geochemical changes alter the hydrodynamic behavior of the medium, at least in theory. The debate about reactive transport in heterogeneous media has started only recently (e.g. Tompson and Jackson (1996)).

Assuming that the programs are highly optimized, computer power still remains a limiting factor in reactive transport modeling. As always, there is a trade-off between computing time and memory resources but reactive transport models are intrinsically computation-intensive. In order to reduce the total CPU time, it is important to know which part of the model is using it. Therefore, several profiling tests have been carried out with HYTEC. For a simple case study (dissolution front of quartz in a sand-column system), ~67 % of the total CPU time is spent on geochemical calculations (this percentage is slightly increased, ~69 %, if dissolution kinetics are used). For more complex geochemical systems, this percentage tends to increase to 87 % (diffusive transport with a sequence of precipitation/dissolution fronts), up to ~99 % for very complex systems with mixed redox/precipitation/cation-exchange reactions. Similar values have been reported in the literature, ranging from 85 to 95

% for relatively simple systems with HYDROGEOCHEM (Yeh and Tripathi 1991) up to 99.9 % for more complex calculations with DYNAMIX (Liu and Narashimhan 1989).

Profiling of HYTEC shows that 75 to 85 % of the CPU time is used to evaluate logarithmic functions, which can hardly be amended programmatically. Nevertheless, considerable reduction of the calculation time can be achieved by using parallel computing techniques. This requires a reactive transport model based on the Sequential Iterative Approach. In theory, parallelization of this kind of model may lead to a gain in normalized CPU time (normalized by n , the number of processors) of n —minus the CPU time needed for communication— for very complex systems.

6 Conclusions and future directions

Geochemical interactions such as speciation, precipitation, dissolution, cation exchange and redox reactions are closely connected with the hydrodynamic regime, especially when the reactions are kinetically controlled. Reactive transport models offer the means of studying geochemically complex, natural systems in their dynamic context, in contrast to closed, static systems. They are invaluable tools to understand the near-field as a whole, as shown by the examples in this study and in an increasing number of recent publications (e.g., Arcos et al. (1998), Lichtner et al. (1998), Bateman et al. (1999), Lucille et al. (1999) Trotignon et al. (1999)). The combined use of modeling and experimental data is an effective method of achieving a conceptual and quantitative understanding of individual reaction pathways (van Cappellen and Gaillard 1996).

Today, reactive transport models have reached a stage where they are able to correctly simulate dynamic laboratory experiments and field observations, including many simultaneously occurring chemical processes for hundreds of species. Progress has also been made with regard to the mathematical part of the problem, thus reducing computation time and increasing numerical stability. Among the several numerical methods listed here, the Sequential Iterative Approach (SIA) has major advantages. First, it can be used to build the overall model from individual models: a transport model, a geochemical model and an interface for the coupling procedure. Therefore, development and maintenance can be distributed among a team of scientists. Secondly, the SIA is quite stable and ready for use for a massively parallel implementation. However, the problem of stiffness (i.e. the occasional need for small time steps) remains: more research is required to, hopefully, solve this problem.

Progress is needed in order to take heterogeneity into account. The aqueous background chemistry varies in time and space as a function of the mineral buffers of the rock. The geochemical composition of the solid phase is heterogeneous at dif-

ferent scales. First, the waste confinement materials and near-field barriers are intrusions into the natural rock and introduce near-field heterogeneity. Furthermore, the mineralogical composition of the host rock is heterogeneous at all scales, from the microscopic (e.g. fracture infill material, pore surface mineralogy) to the megascopic (geological facies) scale. Very few reactive transport models account for spatial heterogeneities.

Even fewer models are able to quantify the impact of precipitation and dissolution on the hydrodynamic behavior (via medium properties such as porosity and permeability), which is an important element in the performance assessment of near-field barriers. Inversely, the porosity and permeability of near-field barriers or geological media are important for their chemical longevity (Berner 1998). The current progress in reactive transport modeling brings this important facet of performance assessment within reach. It is hoped and expected that future research concerning nuclear waste repositories will include this type of modeling as part of the overall performance assessment of the multi-barrier system.

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References

- Allison, J., D. Brown, and J. Nova-Gradac (1990). *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0 user's manual*. Athens: US Environ. Prot. Agency.
- Appelo, C. and D. Parkhurst (1998). Enhancements to the geochemical model PHREEQC-1D transport and reaction kinetics. In Arehart and Hulston (Eds.), *Water-Rock Interaction*, Rotterdam, NL, pp. 873-876. Balkema.
- Appelo, C. and D. Postma (1993). *Geochemistry, groundwater and pollution*. Rotterdam, Holland: A.A. Balkema.
- Arcos, D., J. Bruno, and L. Duro (1998). Geochemical modelling of groundwater/bentonite interaction for waste disposal systems. In Arehart and Hulston (Eds.), *Water-Rock Interaction*, Rotterdam. Balkema.

- Bateman, K., P. Coombs, D. Noy, J. Pearce, P. Wetton, A. Haworth, and C. Linklater (1999). Experimental simulation of the alkaline disturbed zone around a cementitious radioactive waste repository: numerical modelling and column experiments. In *Chemical Containment of Waste in the Geosphere*, Volume 157, pp. 183–194. Geological Society of London.
- Bear, J. (1972). *Dynamics of fluids in porous media*. New York: Dover Publications, inc.
- Berner, U. (1998). Geochemical modelling of repository systems: limitations of the thermodynamic approach. *Radiochim. Acta* 82, 423–428.
- Bethke, C. (1994). *The Geochemist's WorkbenchTM. A users' guide to Rxn, Act2, Tact, React and Gtplot*. University of Illinois.
- Bethke, C. (1996). *Geochemical Reaction Modeling*. Oxford Press.
- Bethke, C. (1997). Modeling transport in reacting geochemical systems. *Comptes Rendus de l'Académie des Sciences* 324, 513–528.
- Bildstein, O. (1998). Modélisation géochimique des interactions eau-gaz-roche. Application à la diagenèse minérale dans les réservoirs géologiques. Master's thesis, Université Louis Pasteur, Strasbourg, France.
- Bolt, G. and W. V. Riemsdijk (1987). Surface chemical processes in soil. In W. Stumm (Ed.), *Aquatic surface chemistry. Chemical processes at the particle-water interface*, Chapter 6, pp. 127–164. John Wiley & Sons.
- Bouchard, D., A. Wood, M. Campbell, P. Nkedi-Kizza, and P. Rao (1988). Sorption nonequilibrium during solute transport. *J. Contam. Hydrol.* 2, 209–223.
- Bruno, J., J. de Pablo, L. Duro, and E. Figuerola (1995). Experimental study and modeling of the U(VI)-Fe(OH)₃ surface precipitation/coprecipitation equilibria. *Geochimica et Cosmochimica Acta* 59(20), 4113–4123.
- Brusseau, M. (1992). Nonequilibrium transport of organic chemicals: the impact of pore-water velocity. *J. Contam. Hydrol.* 9, 353–368.
- Bäverman, C., B. Strömbert, L. Moreno, and I. Neretnieks (1999). CHEMFRONTS: a coupled geochemical and transport simulation tool. *J. Contam. Hydrol.* 36, 333–351.
- Cederberg, G., R. Street, and J. Leckie (1985). A groundwater mass transport and equilibrium chemistry model for multicomponent systems. *Water Resour. Res.* 21(8), 1095–1104.
- Charlet, L. (1993). Cation adsorption on oxides and clays: the aluminium case. *Aquatic Science* 55(4), 291–303.

- Cheng, H.-P. and G.-T. Yeh (1998). Development and demonstrative application of a 3-D numerical model of subsurface flow, heat transfer, and reactive chemical transport: 3DHYDROGEOCHEM. *J. Contam. Hydrol.* *34*, 47–83.
- Cranga, M., L. Trotignon, C. Martial, and E. Castelier (1998). Simulation of the evolution of a clay engineered barrier by interaction with granitic groundwater: dynamics and characteristic timescales. In *Min.Res.Soc.Symp.*, Volume 506. Materials Research Society.
- Cross, J., A. Haworth, I. Neretnieks, S. Sharland, and C. Tweed (1991). Modelling of redox front and uranium movement in a uranium mine at Poços de Caldas. *Radiochimica Acta* *52/53*, 445–451.
- de Marsily, G. (1986). *Quantitative Hydrology*. Academic Press, London.
- de Windt, L., J. Cabrera, and J.-Y. Boisson (1999). Radioactive waste containment in indurated claystones: comparison between the chemical containment properties of matrix and fractures. In *Chemical Containment of Waste in the Geosphere*, Volume 157, pp. 167–181. Geological Society of London.
- Dzombak, D. and F. Morel (1990). *Surface Complexation Modeling. Hydrous Ferric Oxide*. New York: John Wiley & Sons.
- Gallo, Y. L., O. Bildstein, and E. Brosse (1998). Coupled reaction-flow modeling of diagenetic changes in reservoir permeability, porosity and mineral compositions. *Journal of Hydrology* *209*, 366–388.
- Goblet, P. (1989). Programme METIS: Simulation d'écoulement et de transport miscible en milieu poreux et fracturé. Technical Report LHM/RD/89/23, CIG, École des Mines de Paris, Fontainebleau, France.
- Gérard, F., A. Clément, and B. Fritz (1998). Numerical validation of a Eulerian hydrochemical code using a 1D multisolute mass transport system involving heterogeneous kinetically controlled reactions. *J. Contam. Hydrol.* *30*, 201–216.
- Grenthe, I., V. Plyasunov, and K. Spahiu (1997). Estimations of medium effects on thermodynamic data. In I. Grenthe and I. Puigdomenech (Eds.), *Modelling in aquatic chemistry*, Chapter IX, pp. 325–426. OECD Publications.
- Grenthe, I., W. Stumm, M. Laaksuharju, A. Nilsson, and P. Wikbert (1992). Redox potentials and redox reactions in deep groundwater systems. *Chem. Geol.* *98*, 131–150.
- Keating, E. and J. Bahr (1998). Reactive transport modeling of redox geochemistry: approaches to chemical disequilibrium and reaction rate estimation at a site in northern Wisconsin. *Water Resour. Res.* *34* (12), 3573–3584.
- Lasaga, A. (1984). Chemical kinetics of water-rock interactions. *J. Geoph. Res.* *89*, 4009–4025.

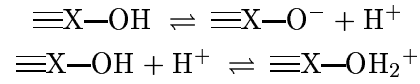
- Lichtner, P. (1996). Continuum formulation of multicomponent-multiphase reactive transport. In P. Lichtner, C. Steefel, and E. Oelkers (Eds.), *Reactive Transport in Porous Media*, Volume 34 of *Reviews in Mineralogy*, Chapter 1, pp. 1–81. Mineralogical society of America.
- Lichtner, P., R. Pabalan, and C. Steefel (1998). Model calculations of porosity reduction resulting from cement-tuff diffusive interaction. In *Mat. Res. Soc. Symp. Proc.*, Volume 506, pp. 709–718. Materials Research Society.
- Liu, C. and T. Narashimhan (1989). Redox-controlled multiple-species reactive chemical transport. 2 Verification and application. *Water Resour. Res.* 25(5), 883–910.
- Lucille, P., A. Burnol, and P. Ollar (1999). Geochemical compatibility of near field materials in terms of radionuclide retention properties. In *Scientific Basis for Nuclear Waste Management*, in print.
- Madé, B., A. Clément, and B. Fritz (1994). Modeling mineral/solution interactions: the thermodynamic and kinetic code KINDISP. *Computer & Geosciences* 20(9), 1347–1363.
- McNab, W. and T. Narasimhan (1994). Modeling reactive transport of organic compounds in groundwater using a partial redox disequilibrium approach. *Water Resour. Res.* 30(9), 2619–2635.
- Miller, C. and L. Benson (1983). Simulation of solute transport in a chemically reactive heterogeneous system: model development and application. *Water Resour. Res.* 19(2), 381–391.
- Morel, F. and J. Hering (1993). *Principles and Applications of Aquatic Chemistry*. New York: John Wiley & Sons Inc.
- Moulin, C. (1996). Logiciel de qualité de l'eau SUBIEF, version 3.1, manuel de l'utilisateur. Technical Report HE-43/95/054/B, Électricité de France (EDF).
- Noorishad, J., C. Carnahan, and L. Benson (1989). Simulation of fractionation of C-13 during nonequilibrium reactive solute transport in geologic systems: formulation and example calculation. *Water Resour. Res.* 25(4), 754–756.
- Ollar, P., P. Lucille, and A. Burnol (1997). Architecture du code couplé chimie-transport CHEMTRAP. Exercices d'application et programme de travail. Technical Report HT-45/97/027/B, EDF-LNH, Chatou, France.
- Parkhurst, D., D. Thorstenson, and L. Plummer (1980). PHREEQE, a computer program for geochemical calculations. Water-Resources Investigations 80-96, U.S. Geological Survey.

- Parkhurst, D. (1995). *A users guide to PHREEQC: a computer program for specification, reaction-path, advective-transport and inverse geochemical calculations*. Lakewood, Colorado: U.S. Geological Survey.
- Pfingsten, W. (1994). Modular coupling of transport and chemistry: theory and model applications. PSI-Bericht 94-15, PSI.
- Pruess, K. (1991). TOUGH2: a general numerical simulator for multiphase fluid and heat flow. Technical Report LBL-29400, Lawrence Berkeley Laboratory, CA, USA.
- Rea, R. and G. Parks (1990). Numerical simulation of coadsorption of ionic surfactants with inorganic ions on quartz. In *Chemical modeling in aqueous systems II*, ACS symposium series 416, pp. 260–271. American Chem. Society.
- Righetto, L., G. Aximonti, T. Missana, and G. Bidoglio (1995). The triple layer model revised. *Colloids and Surfaces. A: Physicochemical Engineering Aspects* 95 9, 141–157.
- Schäfer, D., W. Schäfer, and W. Kinzelbach (1998). Simulation of reactive processes related to biodegradation in aquifers. 1. Structure of the three-dimensional reactive transport model. *J. Contam. Hydrol.* 31, 167–186.
- Soetaert, K., P. Herman, and J. Middelburg (1996). A model of early diagenetic processes from shelf to abyssal depths. *Geochim Cosmochim Acta* 60, 1019–1040.
- Sposito, G. (1994). *Chemical equilibria and kinetics in soils*. Oxford University Press.
- Sposito, G. and C. LeVesque (1985). Sodium-calcium-magnesium exchange on Silver Hill illite. *Soil Sci. Soc. Am. J.* 49, 1153–1159.
- Steeffel, C. and A. Lasaga (1994). A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *American Journal of Science* 294, 529–592.
- Steeffel, C. and K. MacQuarrie (1996). Approaches to modeling of reactive transport in porous media. In P. Lichtner, C. Steefel, and E. Oelkers (Eds.), *Reactive Transport in Porous Media*, Volume 34 of *Reviews in Mineralogy*, Chapter 2, pp. 83–129. Mineralogical society of America.
- Stoessell, R. (1988). 25 °C and 1 atm dissolution experiments for sepiolite and kerolite. *Geochimica et Cosmochimica Acta* 52, 365–374.
- Thiez, P. L. and P. Lemonnier (1990). An in-situ combustion reservoir simulator with a new representation of chemical reactions. *SPE Res. Eng.* 9, 285–292.

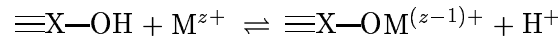
- Tiffreau, C., J. Lützenkirchen, and P. Behra (1995). Modeling the adsorption of mercury(II) on (hydr)oxides. *J. Colloid Interface Sci.* 172, 82–93.
- Tompson, A. and K. Jackson (1996). Reactive transport in heterogeneous systems. In P. Lichtner, C. Steefel, and E. Oelkers (Eds.), *Reactive Transport in Porous Media*, Volume 34 of *Reviews in Mineralogy*, Chapter 6, pp. 269–310. Mineralogical Society of America.
- Trotignon, L., M.-H. Faure, M. Cranga, and H. Peycelon (1999). Numerical simulation of the interaction between granitic groundwater, engineered clay barrier and iron canister. In *Scientific Basis for Nuclear Waste Management, in print*.
- van Cappellen, P. and J. Gaillard (1996). Biogeochemical dynamics in aquatic sediments. In P. Lichtner, C. Steefel, and E. Oelkers (Eds.), *Reactive Transport in Porous Media*, Volume 34 of *Reviews in Mineralogy*, Chapter 8, pp. 335–379. Mineralogical society of America.
- van Cappellen, P. and Y. Wang (1996). Cycling of iron and manganese in surface sediments: a general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron and manganese. *American Journal of Science* 296, 197–243.
- van der Lee, J. (1997a, January). HYTEC, un modèle couplé hydro-géochimique de migration de polluants et de colloïdes. Technical Report LHM/RD/97/02, CIG, École des Mines de Paris, Fontainebleau, France.
- van der Lee, J. (1997b, February). Mechanistic modelling of heavy metal mobility in natural sand. Technical Report LHM/RD/97/02, CIG, École des Mines de Paris, Fontainebleau, France.
- van der Lee, J. (1997c). *Modélisation du comportement géochimique et du transport des radionucléides en présence de colloïdes*. Ph. D. thesis, École des Mines de Paris, Paris, France.
- van der Lee, J. (1998, September). Thermodynamic and mathematical concepts of CHESS. Technical Report LHM/RD/98/39, CIG, École des Mines de Paris, Fontainebleau, France.
- Vinsot, A. and A. Coudrain-Ribstein (1989). Élaboration et validation expérimentale d’une méthode de résolution du couplage entre un modèle géochimique et un modèle de transport d’éléments en solution. Nuclear Science and Technology EUR 12290 FR, Commission of the European Communities (CEC).
- Walter, A., E. Frind, D. Blowes, C. Ptacek, and J. Molson (1994). Modeling of multicomponent reactive transport in groundwater. 1. Model development and evaluation. *Water Resour. Res.* 30(11), 3137–3148.

- Wang, L., P. de Cannière, P. Lolivier, and W. Zhou (1997). Interaction of radionuclides with Boom Clay components: towards a mechanistic model. In *Feasibility and Acceptability of Nuclear Waste Disposal in the Boom Clay formation*, Number BLG-726 in Topical Day: Waste and Disposal Unit, pp. 77–85. SCK·CEN.
- Warwick, P., A. Hall, V. Pashely, J. van der Lee, and A. Maes (1998). Zinc and cadmium mobility in sands: effects of pH, speciation, cation exchange capacity (CEC), humic acid and metal ions. *Chemosphere* 36(10), 2283–2290.
- Westall, J., J. Zachary, and F. Morel (1986). MINEQL - A computer program for the calculation of the chemical equilibrium composition of aqueous systems. Technical Report 86-01, Department of chemistry, Oregon State University.
- Wolery, T. (1992). *EQ3/6: A software package for geochemical modelling of aqueous systems: package overview and installation guide (version 7.0)* (UCRL-MA-110662 PT I ed.). Lawrence Livermore National Laboratory.
- Xu, T., K. Pruess, and G. Brimhall (1999). An improved equilibrium-kinetics speciation algorithm for redox reactions in variably saturated subsurface flow systems. *Computers & Geosciences* 25, 655–666.
- Yabusaki, S., C. Steefel, and B. Wood (1998). Multidimensional, multicomponent, subsurface, reactive transport in nonuniform velocity fields: code verification using an advective reactive streamtube approach. *J. Contam. Hydrol.* 30, 299–331.
- Yeh, G. and V. Tripathi (1989). A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.* 25(1), 93–108.
- Yeh, G. and V. Tripathi (1991). A model for simulating transport of reactive multispecies components: model development and demonstration. *Water Resour. Res.* 27(12), 3075–3094.

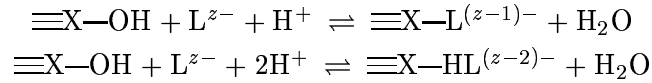
1. acid-base reactions:



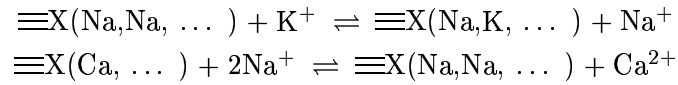
2. metal complexation:



3. ligand complexation:



4. ion exchange:



5. surface precipitation:

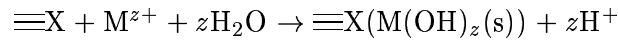


Table 1: Different interface-reaction models expressed in terms of mole balance equations for metals (M^{z+}) and ligands (L^{z-}). The surface corresponds to a hypothetical solid phase formed by species X and, according to a generally accepted formalism, denoted $\equiv\text{X}$.

code	geochemistry	transport	
CHEMFRONTS ¹	–	–	1D
CHEMTRAP ²	CHESS ³	SUBIEF ⁴	1D
CHEQMATE ⁵	PHREEQE ⁶	–	1D
DIAPHORE ⁷	NEWKIN ⁸	SARIP ⁹	1D
DYNAMIX ¹⁰	PHREEQE ⁶	–	1D
HYDROGEOCHEM ¹¹	–	–	1D
3DHYDROGEOCHEM ¹²	–	–	1,2,3D
HYTEC ¹³	CHESS ³	RT1D, METIS ¹⁴	1,2D
KIRMAT ¹⁵	KINDISP ¹⁶	–	1D
MCTRACKER ¹⁷	–	–	3D
MINTRAN ¹⁸	MINTEQA2 ¹⁹	PLUME2D	1,2D
PHREEQC ²⁰	PHREEQE ⁶	–	1D
TOUGHREACT ²¹	REACT ²²	TOUGH2 ²³	1,2,3D
CHMTRNS ²⁴	PHREEQE ⁶	–	1D
XT ²⁵	REACT ²⁶	–	1,2D

- | | |
|---------------------------------|----------------------------------|
| 1 : Bäverman et al. (1999) | 14 : Goblet (1989) |
| 2 : Ollar et al. (1997) | 15 : Gérard et al. (1998) |
| 3 : van der Lee (1998) | 16 : Madé et al. (1994) |
| 4 : Moulin (1996) | 17 : Yabusaki et al. (1998) |
| 5 : Cross et al. (1991) | 18 : Walter et al. (1994) |
| 6 : Parkhurst et al. (1980) | 19 : Allison et al. (1990) |
| 7 : Gallo et al. (1998) | 20 : Appelo and Parkhurst (1998) |
| 8 : Bildstein (1998) | 21 : Xu et al. (1999) |
| 9 : Thiez and Lemonnier (1990) | 22 : Stoessell (1988) |
| 10 : Liu and Narashimhan (1989) | 23 : Pruess (1991) |
| 11 : Yeh and Tripathi (1991) | 24 : Noorishad et al. (1989) |
| 12 : Cheng and Yeh (1998) | 25 : Bethke (1997) |
| 13 : van der Lee (1997a) | 26 : Bethke (1994) |

Table 2: Extract of reactive transport models developed and published over the past decade. ‘–’ indicates an integrated module, not available as a separate model. This list is not exhaustive: in particular, mixing-cell models are not included.

	Clay-rock	FoCa
Mineralogy		
Clay minerals	60 %	80%
Quartz	15 %	7 %
Calcite	15 %	1.5 %
Pyrite	2.5 %	-
Goethite	-	6 %
Fluorite	0.3 %	-
Gypsum	-	0.5 %
CEC	10 meq/100g (1 exchange site)	75 meq/100g (3 exchange sites)
Hydrochemistry		
pH	7.4	8.1
redox	$Eh \simeq -0.25$ V	fug $O_2=0.2$
Ionic strength	0.2	0.06
Water type	Na-Cl	Na-Ca-SO ₄ ²⁻
Hydrodynamic		
D _{eff}	1.3×10^{-11} m ² /s	1.3×10^{-11} m ² /s
Porosity	30 %	30 %

Table 3: Main characteristics of the clay-rock and FoCa barrier for the near-field simulations. The FoCa composition is taken from Cranga et al. (1998), the clay-rock composition is adapted from the Tournemire clay formation (de Windt et al. 1999).

Concrete		Clay	
Portlandite	41	Montmorillonite-Na	12.3
CSH(1.8)	25	Quartz	14.8
Ettringite	0.65	K-Feldspar	1.51
MonoSulfoAl	0.65	Calcite	0.8
		Kaolinite	0.2

Table 4: Mineralogical composition and (total) concentrations (molar) used for the simulation shown in Figure 4.

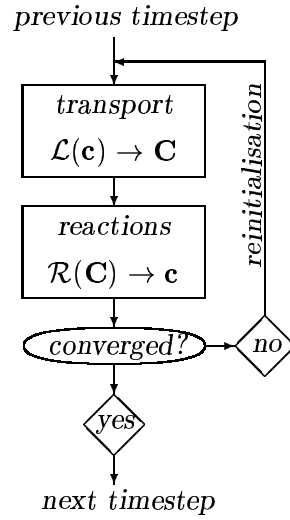


Figure 1: Diagram of consecutive actions within one time step according to the Sequential Iterative Approach. \mathbf{C} denotes the total concentrations, \mathbf{c} the mobile concentrations, \mathcal{L} the transport operator (hydrology) and \mathcal{R} the reaction operator (geochemistry).

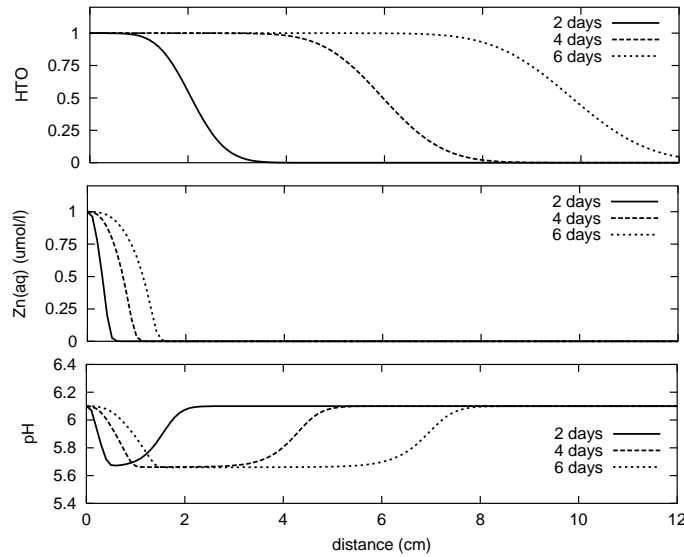


Figure 2: Fronts of a perfect tracer (HTO), aqueous Zn and pH as a result of the injection of 1 μ molar $\text{ZnCl}_2(\text{aq})$, 50 mmolar $\text{NaCl}(\text{aq})$ solution into a quartz column.

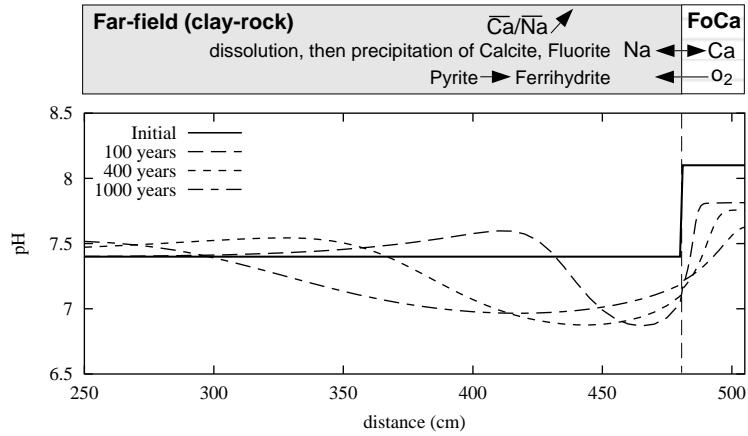


Figure 3: Evolution of pH inside the barriers as a function of time.

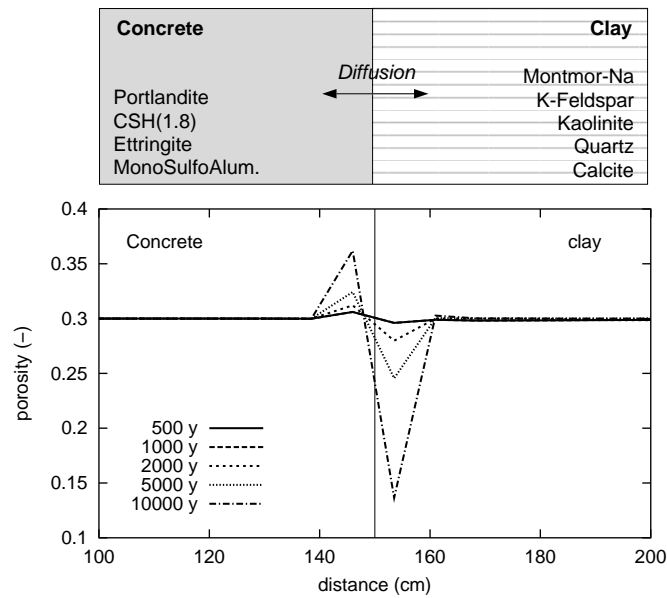


Figure 4: Variation of the porosity of the clay- and concrete barriers as a function of time, simulated by HYTEC.