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Reactive chemical transport within engineered barriers

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Abstract

We consider fully coupled geochemical process systems, and show how they may be cast as differential algebraic systems amenable to numerical solution.

Considering reactive transport within engineered barriers, we motivate problems: (1) involving (some) kinetic reactions; (2) in two or more spatial dimensions; (3) incorporating spatial heterogeneity; and (4) with full coupling.

The examples considered illustrate the possible treatment of spatial heterogeneity (which causes both channelled flow and stagnant water); the treatment of air–water interfaces as moving-boundaries; corrosion at interfaces; nonlinear feedback when the geochemical and flow problems are full coupled, and the formation of fingering patterns.

Our preliminary calculations indicate that such problems are numerically tractable. However, verification and the availability of suitable data remain outstanding issues. Even though these problems are nonlinear, there is range of analytical tools available, and some aspects of the solution can be known quantitatively as well as qualitatively.

1. Introduction

In modelling geochemical reactive transport processes, assumptions of instantaneous equilibration, pseudo steady states, or geometrical symmetry are common. For example, within performance assessment programmes, instantaneous elemental solubility limits or adsorption equilibrium partitions are often imposed at a conceptual level. Thus little if

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any consideration is made of the transient behaviour and the timescales at which such concepts are invalid; or how these assumptions may bias the results of the assessment. In more complex geochemical systems, where invading water is in disequilibrium with rock minerals or emplaced barriers, and the suite of chemistry is very large, the imposition of equilibrium assumptions can be even more critical and the timescales associated with transients are significant.

In many available models and codes, chemical reactions and transport phenomena are dealt with by a two-stage method in which the chemistry is equilibrated instantaneously following discrete perturbations, representing the transport fluxes of individual species. Chemical equilibrium databases are often accessed by such methods regardless of the timescales governing the particular phenomena under consideration.

Recent studies have concluded (Bruno et al., 1992) that geochemical transport models must incorporate transient (kinetic) effects, as well as the full coupling of chemical processes to transport processes, via fluid displacement due to volumetric changes within the mineralogy of the host media.

From a theoretical point of view, Grindrod (1991, 1993) and Ortoleva and Chen (1992) among others have long pointed out the restriction that ignoring such processes places upon the geochemical system models and their solutions. Indeed there is a large literature concerning reaction diffusion–advection systems detailing how the coupling of such processes can produce a wealth of structural pattern in both space and time. The key point is that there may be critical periods within the evolution of a system where some of the chemical reactions cannot be equilibrated instantaneously: instead they evolve on non-negligible timescales compared to those associated with the transport phenomena. Sharp transition layers, for example, may develop and propagate, with quiescent states to either side.

Until recent years, this remained a largely academic subject owing to the computational cost of solving the full equations, and the relative level of sophistication required of the spatially distributed chemical systems under consideration. Data availability was also a problem. However, more recently, and particularly within the environmental sciences, coupled processes and heterogeneous systems have begun to be considered.

The complexibility of the environment calls for a detailed understanding of geochemical processes (fluid flow, solute transport, chemistry, and so on), yet some phenomena require coupling between such processes in order to be modelled adequately, or even at all. Thus there is a growing interest in reactive transport models allowing for disequilibrium on model timescales where necessary.

Recognizing this fact, JGC and Intera have jointly developed expertise and a code, ARASE (Rough Wave), as a tool for analyzing problems in the environmental sciences.

The situation in two or more spatial dimensions is of central interest, since even for smooth initially distributions of solids and solutes, patterns can spontaneously arise and near plane waves can develop fingers (Ortoleva and Chen, 1992), as a result of the full coupling of the reactive transport to the fluid flow.

The ability of coupled nonlinear models to exhibit spatial patterns is of key importance to performance assessment since implicit assumptions of symmetry can bias calculations and preclude behaviour such as fingering or pitting corrosion. This is made even more critical by the presence of spatial heterogeneities within the host media. All materials are heterogeneous at some scales, and even, relatively uniform media may be subject to heterogeneous boundary conditions as a result of external features. Thus we must consider

(1) natural heterogeneity,
(2) dynamic (kinetic) mineral reactions,
(3) solute transport,

all coupled through flow, transport and mineral alteration. Hence, even for initially well-characterized media, assumptions of simple uniform geometry for flow, or homogeneity, or equilibration, may be far from the reality, and can bias our thinking as well as results.

Of course it is one thing to draw cartoons of coupled processes, but another to provide a mathematical model. Hence the spirit of this paper is to discuss what can be done (at present) and indicate the direction of our future research with ARASE.

Looking ahead it is important to collect together a number of well-documented example applications. At some point a cross-model verification exercise would be useful, and examples exhibiting coupled process behaviour unavailable within one-dimensional equilibrium models should be of central interest.

Any attempts to treat the kinetic behaviour of reactions raises questions about the availability and reliability of data. Clearly models such as ARASE will ultimately need to be linked to referencable data. In the first place though it is most important to compare results to well-defined experiments and as to whether the models are adequate to explain the kinetic behaviour encountered. In this paper we wish to demonstrate the type of calculations which maybe made, by examining some specific examples.

2. Some problems

ARASE has been developed with a number of problems in mind. We briefly describe these.

2.1. Fully coupled precipitation / dissolution problems

Here the porous medium is characterized by a few key reactive mineral species. Interaction with incoming pore water causes porosity changes resulting in further fluid displacement and hence advection. Preliminary calculations have been run in order to verify the solution procedure. Previous one-dimensional calculations modelling the dissolution processes within cementitious environment (fully coupled to fluid flow) have been used for verification exercises. For example, in Noy (1990) such a nonlinear model for the reaction of anorthite with quartz to form laumontite is considered. ARASE obtained results, see Fig. 1 and 2, identical to those in Noy (1990) using a much smaller computer (owing to the efficiency of the variable order, variable time-stepping solver for systems of differential and algebraic equations; Thomas, 1993).

It is known that in two dimensions, fully coupled systems can produce fingering patterns (Ortoleva and Chen, 1992; Grindrod, 1993). Hence, ARASE will be applied to model fully coupled problems in two-dimensional regions.

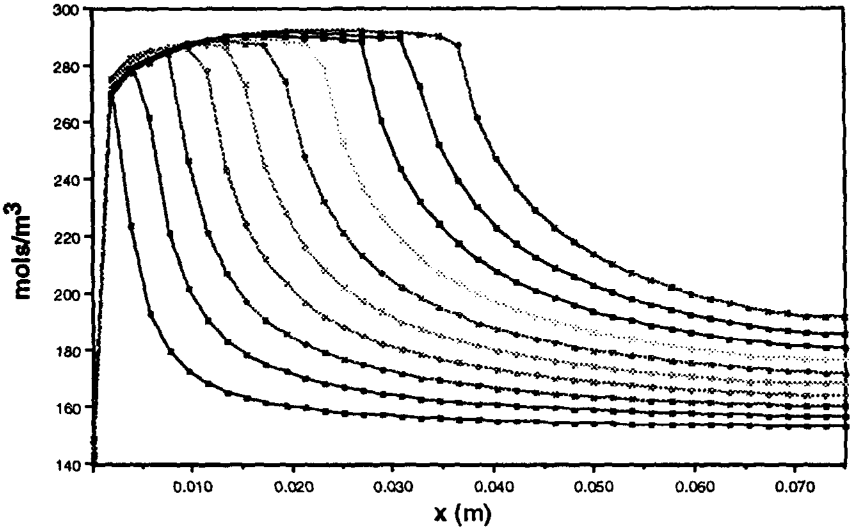


Fig. 1. Concentration of laumontite ($CaAl_2Si_4O \cdot 2.4H_2O$) at times $1 \cdot 10^6$, $2 \cdot 10^6$, $3 \cdot 10^6$, ..., $1 \cdot 107$ s at positions x along the flow path.

Scalloping or fingering happens when a reactive solute species invades some medium, and the reacted media formed has a lower permeability than the unreacted media. Hence if perturbations to the plane wave geometry form fingers, the flow can become channelled towards the fingertips, and the solute delivered preferentially to these

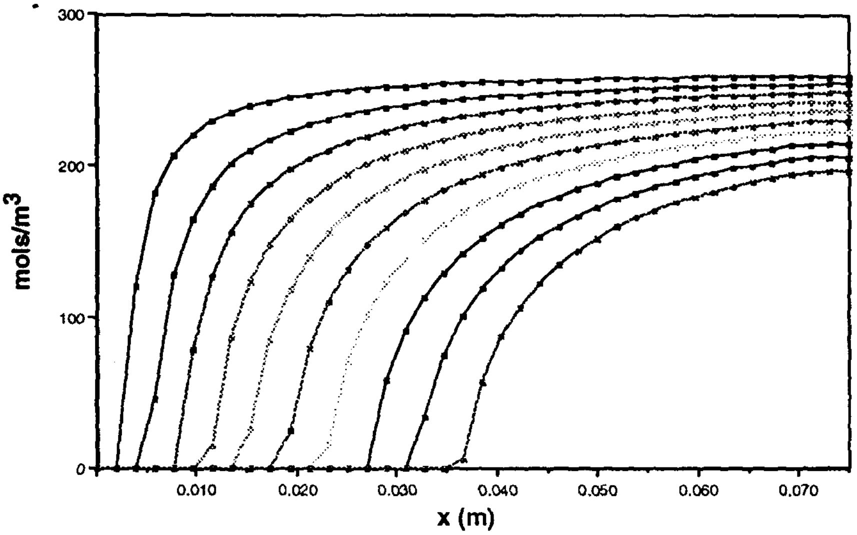


Fig. 2. Concentration of anorthite ($CaAl_2Si_2O_8$) at times $1 \cdot 10^6$, $2 \cdot 10^6$, $3 \cdot 10^6$, ..., $1 \cdot 10^7$ s at positions x along the flow path.

points. This results in further growth to the structure; however, such instability will be diffusion limited and has a characteristic spatial scale.

2.2. Multibarrier geometry

Here the solution domain is partitioned into subregions representing, for example host rock, a clay barrier, and a cement barrier. This results in a large suite of chemistry with spatially discontinuous mineralogy. Heterogeneous initial distributions and permeabilities are generated, along with the consequent channelled flow by employing statistically self-affine fractals (Grindrod and Impey, 1993). These can produce high-resolution details providing preferential flow paths for reactive transport. Hence there are regions of stagnant water; and regions of relatively high flow, which may give rise to geochemical disequilibrium. Since exterior heterogeneity within the host rock yields structured pressure fields, there can be such channelling even in the relatively homogeneous barriers.

Statistically self-affine fractals, defined over a two-dimensional region, yield surfaces which have noninteger dimension between 2 and 3. The higher the dimension, the less smooth are the distributions they represent.

It can be shown that such fields of fractal dimension $3 - H$ (for H between 0 and 1) obey statistical scaling laws which imply the semivariogram behaves like the $2H$-power at small values of separation. Typically permeability fields for crushed or fractured rock have fractal dimensions greater than 2.5, given their non-smoothness, whereas a homogeneous small grained medium like a clay will have a smoother permeability field of fractal dimension close to 2 (two-dimensional surfaces being differentiable). Of course, we only rely on the fractal scaling holding down to the scale of the resolution of the calculation, but not necessarily beyond this cut-off. Similarly, we do not impose it at large spatial scales.

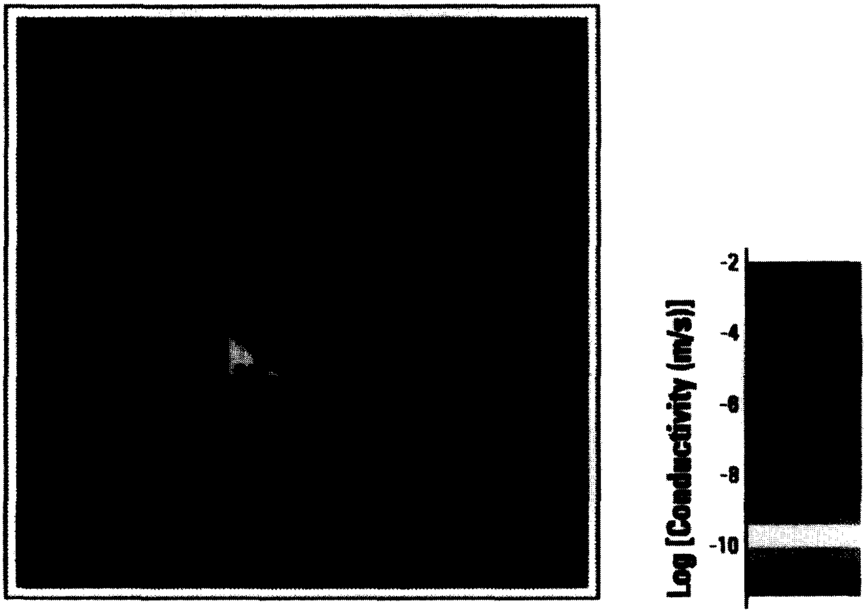
Fig. 3 depicts a typical flow field (modulus of the Darcy velocity) developed for a two-dimensional section through such a multibarrier domain. The outer layer is rock with conductivities between 10^3–10^4 m s^{-1}, and is highly heterogeneous (of fractal dimension 2.75); the middle layer represents more homogeneous compacted clay with conductivities 10^7–10^8 m s^{-1} (fractal dimension 2.1); the inner layer represents concrete and is slightly heterogeneous with conductivities 10^{10}–10^{11} m s^{-1} (fractal dimension 2.3).

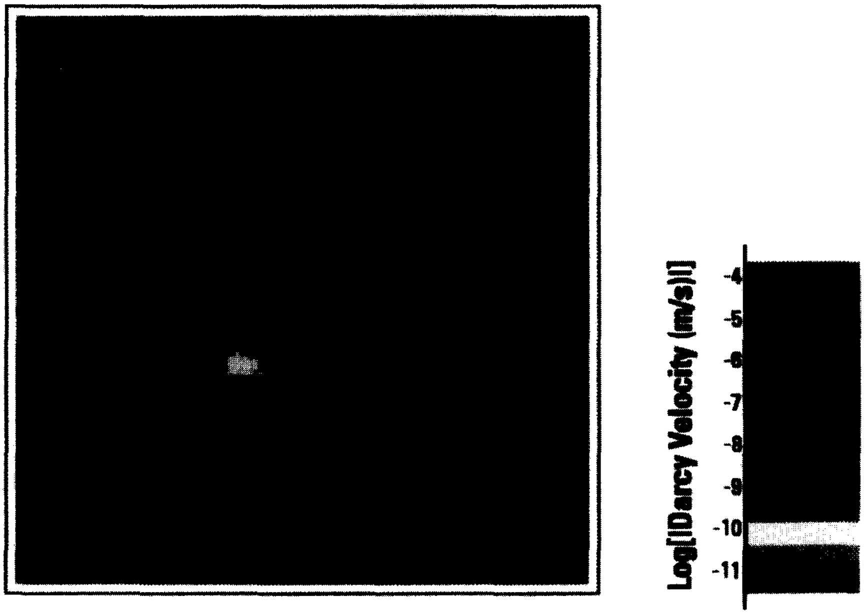
In examining such systems it is the aim to consider the relative timescales associated with the mineral reactions and the fast channelled flow. Hence it is expected that disequilibrium and the consequence of the coupled processes will be observed within the key flow paths, rather than uniformly throughout the medium.

2.3. Geochemical transients during and after a buffer saturation phase

Here reactive transport is driven by the saturating behaviour of an initially dry buffer region. Hence the wetting region is enlarging and more and more water is drawn from the exterior.

As an example, let us consider the reactive transport of aqueous and mineral species


Log [Conductivity (m/s)]
-2
-4
-6
-8
-10


Log[|Darcy Velocity (m/s)|]
-4
-5
-6
-7
-8
-9
-10
-11

within the near field of a deep geological radioactive waste repository. We solve for solute and mineral species during and after the resaturation phase of a bentonite buffer. Thus the domain of solution changes in time as more bentonite becomes wetted, and gains access to the aqueous chemistry.

At the moving air–water interface there is a source of both O_2 and carbonate species due to dissolution. At the outer bentonite–rock boundary the aqueous chemistry is held constant (due to the relatively large permeability). Following resaturation both aerobic and anaerobic corrosion of the bentonite–steel interface is possible. The transport component allows for diffusion terms and (resaturation driven) advection. The geometry is assumed here to be radially symmetric, since we are primarily interested in the impact of a moving front end corrosion boundary conditions but this will not be the case in future calculations (Crompton et al., 1995), once we have reviewed the performance of the specified geochemical model.

Examples of output from ARASE are shown in Fig. 4. In each case the chemical species are graphed against radial coordinate r, at times $t = 8, 16, 24, \ldots, 56$ yr.

The bentonite–steel overpack interface is located at $r = 0.5$ m, where corrosion can take place. The bentonite–rock interface is at $r = 1.5$ m. During resaturation (the first 35 years) aqueous solutions are calculated and depicted only at those locations r, which are wet. Note how following resaturation the O_2 plume both diffuses out of the buffer, and is also depleted rapidly at the buffer overpack interface.

In this example we considered a total of 20 aqueous species, 9 mineral species, 13 instantaneous reactions and 9 slow reactions. The relevant components and the chemical reactions are given in Appendix B.

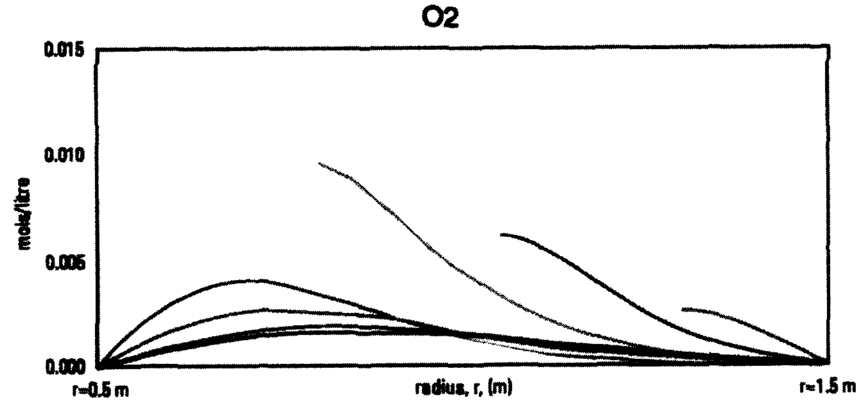
3. Model equations

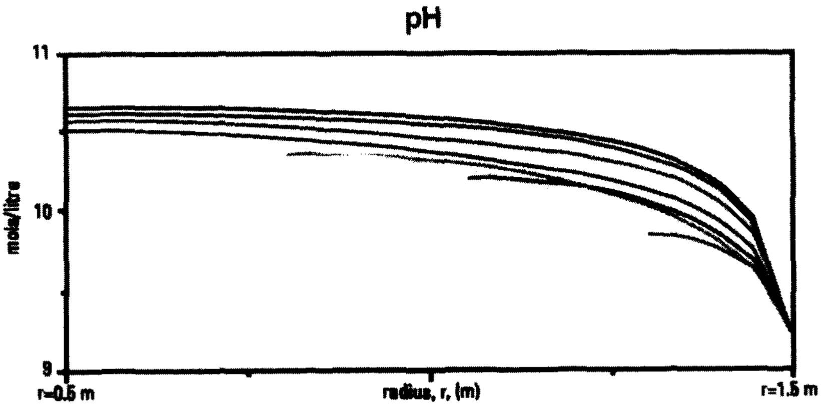
We shall consider reactive transport within a saturated region of a porous medium. Aqueous species are advected by the groundwater flow and may diffuse. Solid species are assumed immobile and the corresponding transport terms are zero. Generalizations to include a mobile solid phase (i.e. colloids) would be straightforward.

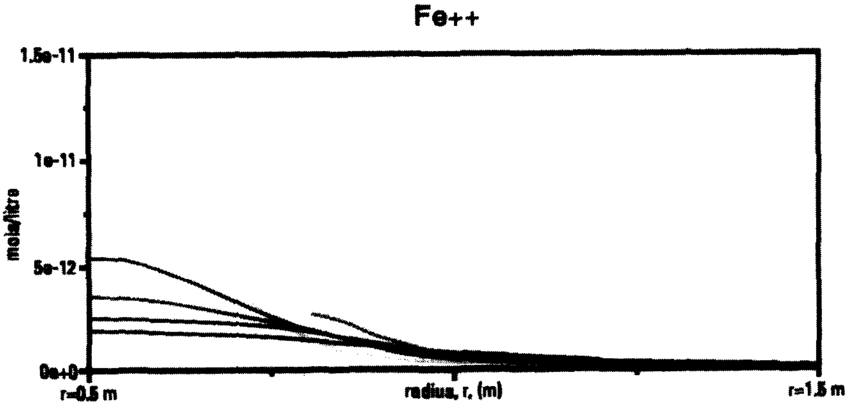
We begin by specifying a system of reaction–diffusion–advection equations for n solute species, with concentrations (moles per unit fluid volume) denoted by $\boldsymbol{u} = (u_1, \ldots, u_n)^T$, and m solid species, with concentrations (moles per unit in situ volume), $w = (w_1, \ldots, w_m)^T$. Both and distributions depend upon spacial location, denoted by $\boldsymbol{x}$, and time, t. Let the porosity be denoted by $\theta = \theta(x,t)$; $\boldsymbol{v}$ will denote the Darcy velocity ($\boldsymbol{v}/\theta$ is the mean fluid velocity).

We shall partition the chemical reactions into fast reactions and slow reactions. Formally, the definition of such terms means that they take place on fast or slow timescales relative to the timescales associated with the transport processes. In practice, the division may be taken to be between solute–solute reactions which rapidly equili-

Fig. 3. Conductivity and modulus of the Darcy velocity for a three-component system: host rock (fractal dimension 2.75)–clay buffer (2.1)–concrete (2.3).


O2
0.015
0.010
0.005
0.000
mole/litre
r=0.5 m
radius, r, (m)
r=1.5 m


pH
11
10
9
mole/litre
r=0.5 m
radius, r, (m)
r=1.5 m


Fe++
1.5e-11
1e-11
5e-12
0e+0
mole/litre
r=0.5 m
radius, r, (m)
r=1.5 m

brate, and precipitation/dissolution reactions affecting, the mineralogy, $\boldsymbol{w}$, which take place more slowly.

Fast reactions will be assumed to be in instantaneous equilibrium whereas slow reactions will be treated kinetically. However, it is instructive to consider this situation as an asymptotic limit of the true dynamic system, since this motivates our set up of the problem, and is essential to obtain the correct set of equations which control the evolution of the resulting constrained system.

We assume that there are p-fast reactions with reaction terms, $\boldsymbol{F}(\boldsymbol{u}) = (F_1, \dots, F_p)^{\mathrm{T}}$ and q slow reactions with reaction rates $\boldsymbol{S}(\boldsymbol{u},\boldsymbol{w}) = (S_1, \dots, S_q)$.

For example, if the jth fast reaction is of the form:

$$\alpha[u_1] + \beta[u_2] \overset{K}{\rightleftharpoons} \gamma[u_3] + \delta[u_4] \tag{1}$$

where α, β, γ and δ are stoichiometric constants, then the reaction proceeds to the right or to the left according to whether the term

$$F_j \equiv -a_1^{\alpha} a_2^{\beta} K + a_3^{\gamma} a_4^{\delta} \tag{2}$$

is positive or negative. Here $a_i = a_i(u_i)$ is the activity of species i (some given function).

We assume that the rate of reaction is given by $R_j F_j$ where R_j is a large positive constant. The reaction becomes instantaneous in the limit $R_j \to \infty$; consequently, the term F_j must tend to zero in this limit providing an equilibrium constraint.

Instantaneous equilibration of fast reactions requires $\boldsymbol{F} = 0$, identically. This is equivalent to assuming that the reactions have a rate which is infinite, so that $\boldsymbol{F}$ approaches zero more rapidly than any other process.

If the jth slow reaction is precipitation/dissolution reaction of the form:

$$\alpha u_1 + \beta u_2 \underset{k_{2,j}}{\overset{k_{1,j}}{\rightleftharpoons}} \gamma w_1 \tag{3}$$

then the corresponding slow kinetic reaction term is

$$S_j = k_{1,j} a_1^{\alpha} a_2^{\beta} + k_{2,j} A(w_1) \tag{4}$$

where $k_{1,j}$ and $k_{2,j}$ are the rates of the forward and back reactions, respectively; and A is the activity of the mineral species (w_1), which depends upon specific surface area (grain size, etc.).

Conservation of mass implies that:

$$(\theta \boldsymbol{u})_t = \boldsymbol{T}(\boldsymbol{u}) + \theta B_{\mathrm{S}} \boldsymbol{S}(\boldsymbol{w},\boldsymbol{u}) + \theta B_{\mathrm{F}} R \boldsymbol{F}(\boldsymbol{u}) \tag{5}$$

Here $\boldsymbol{T}(\boldsymbol{u})$ denotes the net rate of increase in mass per unit volume due to transport of solutes (diffusion and advection); θ is the porosity of the porous medium; $R = \mathrm{diag}(R_1, \dots, R_p)$ is a $(p \times p)$ diagonal matrix of fast reaction rates, and B_{F} and B_{S} are $(n \times p)$ and $(n \times q)$ matrices containing the stoichiometric coefficients of the fast and

Fig. 4. Sample profiles derived from calculating groundwater–bentonite interaction during and after resaturation.

slow reactions, respectively. For example, assuming F_j is given by Eq. 2, the jth column of B_F must be of the form $(\alpha,\beta,-\gamma,-\delta,0,\ldots,0)^{\mathrm{T}}$.

We consider Eq. 5 in the limits $R_1,\ldots,R_n \to \infty$. In doing so we must eliminate the $\boldsymbol{RF}$ terms and so obtain a new system governing the $n-p$ degrees of freedom available in the limit.

We introduce an $n \times (n-p)$ matrix C such that $C^{\mathrm{T}}B_{\mathrm{F}}=0$. This is arranged by choosing columns of C to be an orthogonal set of vectors each of which is orthogonal to the p-dimensional space spanned by the columns of B_{F}. Let $\boldsymbol{c}_i$ denote the ith column of C. The quantities $U_i=\{c\}_i\cdot\boldsymbol{u}$, simple linear combinations of the solute species, are of central interest since these are conserved with respect to all of the fast reactions: notice that the $\boldsymbol{c}_i$'s are completely determined by the stoichiometry of the fast reactions. Hence the U_i's $(i=1,\ldots,n-p)$ provide a set of coordinates within which then fast reactions are eliminated and the slow kinetics and transport processes can be considered. Premultiplying Eq. 5 by C^{T}, and setting $\boldsymbol{U}=(U_1,\ldots,U_{n-p})=C^{\mathrm{T}}\boldsymbol{u}$, we obtain:

$$(\theta+U)_t=C^{\mathrm{T}}\boldsymbol{T}(\boldsymbol{u})+\theta C^{\mathrm{T}}B_{\mathrm{S}}\boldsymbol{S}(\boldsymbol{w},\boldsymbol{u}) \tag{6}$$

Thus the term $\boldsymbol{RF}(\boldsymbol{u})$ has been eliminated and Eq. 6 is valid as any $R_i\to\infty$: that is in the limit that the fast reactions are considered as instantaneous.

Hence at any time $t>0$, we solve Eq. 6 together with the algebraic system:

$$0=\boldsymbol{F}(\boldsymbol{u}) \tag{7}$$

$$0=C^{\mathrm{T}}\boldsymbol{u} \tag{8}$$

which yields $\boldsymbol{u}$ in terms of $\boldsymbol{U}$ (and trivially vice versa).

In general Eq. 6 must be coupled with the equations for the mineral species:

$$\boldsymbol{w}_t=\tilde{B}_{\mathrm{S}}\boldsymbol{S}(\boldsymbol{w},\boldsymbol{u}) \quad (\boldsymbol{w}\geq 0) \tag{9}$$

where $\tilde{B}_{\mathrm{S}}$ denotes the stoichiometry matrix for the mineral precipitation and dissolution reactions.

Finally, the mineralogy distribution may be coupled back to the transport terms $[\boldsymbol{T}(\boldsymbol{u})]$ via the volumetric change in the medium and the displacement of pore water. We have:

$$\theta=g(\boldsymbol{w}) \tag{10}$$

where g is some known function describing porosity in terms of the current mineralogy, and conservation of mass for the pore water implies:

$$\theta_t+\nabla\cdot\boldsymbol{v}=0 \tag{11}$$

where the Darcy velocity $\boldsymbol{v}$ satisfies Darcy's law:

$$\boldsymbol{v}=-k(\theta)\nabla P \tag{12}$$

k is the permeability (porosity dependent) and P is the hydrostatic pressure.

In these terms $\boldsymbol{T}(\boldsymbol{u})=(T_1,\ldots,T_n)$ can be written explicitly as:

$$T_i=\nabla\cdot[\theta D_i\nabla u_i\boldsymbol{v}u_i] \tag{13}$$

where D_i is the diffusion–dispersion tensor for the i^{th} species.

Our approach is to solve Eqs. 6–12, simultaneously employing a nonlinear solver with variable time stepping. In simple situations where θ is assumed to be constant, then $\boldsymbol{v}$ is fixed a priori via Eqs. 11, 12 and 6 is solved with Eqs. 7–9.

Reaction and solute transport takes place within the saturated regions. At boundaries we must impose conditions on the solute species: flux conditions or constant concentrations, for example. At free boundaries where there is a water–gas interface the evolution of the boundary itself must be specified or calculated, as well as any gas dissolution or exsolution as a consequence of the saturation or desaturation of pore space.

These problems fall within a class known as differential and algebraic systems (DAS). Much is known about the numerical solutions of DAS, in particular, that their solvability depends upon an internal classification or index (Brenan et al., 1989). For systems of the kind introduced here a solution method employing a variable time-stepping backward difference formula is suitable (Gear, 1971).

Fully coupled systems of equations have been considered analytically (Chadam et al., 1987; Grindrod, 1993), as well as numerically (Chadam et al., 1987) in two spatially dimensions. The mineralogical (porosity) dependent permeability term can result in the spontaneous growth of fingering patterns: one-dimensional models preclude this by implicit imposition of symmetry.

4. Conclusions

We have examined coupled geochemical process systems, and shown how they may be cast as differential algebraic systems amenable to numerical solution.

The examples considered here were chosen to highlight the impact of spatial heterogeneity in causing channelled flow and stagnant water; the treatment of air–water interfaces as moving-boundaries; nonlinear feedback when the geochemical and flow problems are full coupled, and the formation of fingering patterns.

Preliminary calculations indicate that such problems are tractable (numerically). (However, verification is an issue. For this reason we are currently compiling some test problems which are either documented in the literature (e.g., Noy, 1990), or else are amenable to mathematical analysis. Even though these problems are nonlinear, there is range of analytical tools available, and some aspects of the solution can be known quantitatively as well as qualitatively.

We stress the need to consider problems

(1) involving (some) kinetic reactions;
(2) in two or more spatial dimensions;
(3) incorporating spatial heterogeneity;
(4) with full coupling.

In this way we can make detailed calculations unbiased by standard equilibration assumptions and so on. Hence we can indicate when and where such modelling can be defended, and how system behaviour can be critically modified in certain circumstances.

Appendix A

We briefly state the chemical system model for the anorthite–quartz reaction given in Noy (1990) and solved here using ARASE.

Space precludes the definition of parameters which are the same as in Noy (1990). Chemical reactions considered:

$$\underset{\text{(solid quartz)}}{SiO_2} + 2H_2O \rightleftharpoons H_4SiO_4 \tag{A-1}$$

$$\underset{\text{(solid anorthite)}}{CaAl_2Si_2O_8} + 8H_2O \rightleftharpoons Ca^{2+} + 2H_4SiO_4^0 + 2Al(OH)_4 \tag{A-2}$$

$$\underset{\text{(solid laumontite)}}{CaAl_2Si_4O_1 \cdot 2.4H_2O} + 8H_2O \rightleftharpoons Ca^{2+} + 4H_4SiO_4 + 2Al(OH)_4^- \tag{A-3}$$

Kinetic rate laws are used for all three reactions. The porosity is a function of the mass concentrations of the various solid components. Conservation of fluid mass couples the porosity change to the fluid velocity term, advecting the solute species.

Table 1
List of reactants

Variable	Reactant	Aqueous/solid	Boundary value at $r = 1.5$ m (eq mol L^{-1})
u_1	Z^-	solid	0
u_2	Na+	aqueous	$3.0 \cdot 10^{-3}$
u_3	ZNa	solid	0
u_4	Ca^{2+}	aqueous	$2.84 \cdot 10^{-5}$
u_5	Z_2Ca	solid	0
u_6	CO_3^{2-}	aqueous	$1.4 \cdot 10^{-4}$
u_7	H^+	aqueous	$6.25 \cdot 10^{-10}$
u_8	HCO_3^-	aqueous	$1.9 \cdot ^{-3}$
u_9	O_2	aqueous	0
u_{10}	SO_4^{2-}	aqueous	0
u_{11}	Fe^{2+}	aqueous	$1.07 \cdot 10^{-14}$
u_{12}	Fe^{3+}	aqueous	$3.16 \cdot 10^{-33}$
u_{13}	HS^-	aqueous	0
u_{14}	H_2CO_3	aqueous	$2.68 \cdot 10^{-6}$
u_{15}	$Fe(OH)_3$	solid	1
u_{16}	OH^-	aqueous	$1.58 \cdot 10^{-5}$
u_{17}	$CaCO_3$	solid	1
u_{18}	FeS_2	solid	1
u_{19}	$Fe(OH)_2$	solid	0
u_{20}	Fe_3O_4	solid	0
u_{21}	Fe	solid	0
u_{22}	H_2S	aqueous	0
u_{23}	$CaOH^+$	aqueous	$9.71 \cdot 10^{-9}$
u_{24}	$FeOH^+$	aqueous	$1.13 \cdot 10^{-15}$
u_{25}	$Fe(OH)_2$	aqueous	$1.04 \cdot 10^{-17}$
u_{26}	$FeOH^{2+}$	aqueous	$3.26 \cdot 10^{-26}$
u_{27}	$Fe(OH)_2^+$	aqueous	$1.73 \cdot 10^{-20}$
u_{28}	$Fe(OH)_3$	aqueous	$1.24 \cdot 10^{-17}$
u_{29}	$Fe(OH)_4^-$	aqueous	$4.74 \cdot 10^{-18}$

Appendix B

Here we list the reactants (Table 1) and the reactions (Table 2) modelled using ARASE for the bentonite-resaturation and canister corrosion problem solved in Fig. 4 are listed.

Table 2
Fast and slow reactions

Reaction	Class
$Z^- + Na^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ZNa$	dynamic
$2Z^- + Ca^{2+} \rightleftharpoons Z_2Ca$	instantaneous
$Ca^{2+} + CO_3^{2-} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} CaCO_3$	dynamic
$HCO_3^- \rightleftharpoons H^+ + CO_3^2$	instantaneous
$2FeS_2 + 2H_2O + 7O_2 \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} 4H^+ + 4SO_4^{2-} + 2Fe^{2+}$	dynamic
$Fe(OH)_2 + 2H^+ \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} Fe^{2+} + 2H_2O$	dynamic
$H^+ + HCO_3^- \rightleftharpoons H_2CO^3$	instantaneous
$4Fe^{2+} + O_2 + 4H^+ \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} 4Fe^{3+} + 2H_2O$	dynamic
$Fe^{3+} + 3H_2O \underset{k_{18}}{\overset{k_{17}}{\rightleftharpoons}} Fe(OH)_3 + 3H^+$	dynamic
$H_2O \rightleftharpoons H^+ + OH^-$	instantaneous
$Fe_3O_4 + 8H^+ \underset{k_{22}}{\overset{k_{21}}{\rightleftharpoons}} Fe^{2+} + 2Fe^{3+} + 4H_2O$	dynamic
$FeS_2 + 8H_2O + 14Fe^{3+} \underset{k_{24}}{\overset{k_{23}}{\rightleftharpoons}} 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	dynamic
$H_2S \rightleftharpoons H^+ + HS^-$	instantaneous
$CaOH^+ + H^+ \rightleftharpoons Ca^{2+} + H_2O$	instantaneous
$FeOH^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O$	instantaneous
$Fe(OH)_2 + 2H^+ \rightleftharpoons Fe^{2+} + 2H_2O$	instantaneous
$FeOH_2 + + H^+ \rightleftharpoons Fe^{3+} + H_2O$	instantaneous
$Fe(OH)_2^+ + 2H^+ \rightleftharpoons Fe^{3+} + 2H_2O$	instantaneous
$Fe(OH)_3 + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O$	instantaneous
$Fe(OH)_4^- + 4H^+ \rightleftharpoons Fe^{3+} + 4H_2O$	instantaneous
At the inner boundary:	
$2Fe + O_2 + H_2O \rightarrow 2Fe(OH)_2$	instantaneous
$3Fe + 4H_2O \xrightarrow{k_{an}} Fe_3O_4 + 4H_{2(gas)}$	dynamic

Slow reactions are treated dynamically, whilst fast reactions are assumed to be equilibrated instantaneously, relative to the timescales associated with both the slow reactions and the transport processes. Reaction rates are denoted by lower case k's.

References

Brenan, K.E., Campbell, S.L. and Petzold, L.R., 1989. Numerical Solution of Initial Value Problems in Differential Algebraic Equations. North-Holland Publishing Co., Amsterdam.

Bruno, J., Crawford, M., Fabriol, R., Jamet, Ph., Lang, H., Read, D., Tweed, C. and Warwick, P., 1992. Status review of CHEMVAL2 technical areas. U.K. Dep. Environ., London, Rep. No. DoE/HMIP/RR/93.014, June 1992.

Chadam, J., Merino, E., Ortoleva, P. and Sen, A., 1987. Geochemical self-organization, II: The reactive infiltration instability. Am. J. Sci., 287: 1008–1040.

Crompton, S., Grindrod, P., Takase, H. and Woods, J., 1995. Multibarrier geochemical problems in two spatial dimensions. Proc. 5th Int. Conf. on Chemistry and Migration of Actinides and Fission Products in the Geosphere, Saint-Malo, Sept. 1995.

Gear, C.W., 1971. Simultaneous numerical solution of differential algebraic equations. J. Inst. Electr. Electron. Eng., Trans. Circuit Theory, 18: 89–95.

Grindrod, P., 1991. Patterns and Waves: The Theory and Applications of Reaction Diffusion Equations. Clarendon, Oxford.

Grindrod, P., 1993. Some reactive transport, dispersal and flow problems associated with geological disposal of radioactive waste. In: B.D. Sleeman and R.J. Jarvis (Editors), Ordinary and Partial Differential Equations, Vol. IV. Longman, London.

Grindrod, P. and Impey, M.D., 1993. Application of fractal geometry to geological site characterization. In: A.J. Crilly, R.A. Earnshaw and H. Jones (Editors), Applications of Fractals and Chaos. Springer, Berlin.

Noy, D.J., 1990. PRECIP: A program for coupled groundwater flow and precipitation/dissolution reactions. Nirex Ltd., Harwell, Nirex Safety Stud. Rep. NSS/R275, Aug. 1990.

Ortoleva, P. and Chen, W., 1992. Development of complex reaction front morphologies through nonlinear fluid–rock interaction in modelling, asymptotic and numerical studies. In: W.E. Fitzgibbon and M.F. Wheeler (Editors), Modelling and Analysis of Diffusive and Advective Processes in Geosciences. Siam, Philadelphia, PA.

Thomas, R., 1993. Geochemical Test Cases 1 to 4. Intera Info. Technol. Inc., Henley-on-Thames, Rep., Aug. 1993.