ABSTRACT - We present a synthetic review of some key modeling aspects associated with (a) precipitation / dissolution reactions in carbonate systems and (b) competitive behavior of heavy metals compounds in a well characterized porous system. We start by reviewing some recent advances in theoretical and numerical modeling of complex reactive transport problems, resulting in a methodology conducive to a simple exact expression for the distribution of reaction rates in the presence of homogeneous or heterogeneous reactions under chemical equilibrium (DE SIMONI et alii, 2005, 2007). We then focus on a set of laboratory-scale experiments and show how this methodology can be used to describe the global (integral) reaction rate occurring in a relatively complex, geochemically-active system under the assumption of chemical equilibrium. We model three calcium carbonate dissolution experiments reported in SINGURINDY et alii (2004, 2005), in which saltwater and freshwater were mixed in different proportions. The experimental results are also used to examine the performance of a Darcy-scale flow and reactive transport numerical model, based on the advection-dispersion-reaction equation, to reproduce measured global reaction rates. We then present a comparative analysis of the ability of four alternative models to interpret the set of batch experiments presented by SRIVASTAVA et alii (2006), involving competitive binary-component adsorption studies of cadmium (Cd(II)) and nickel (Ni(II)) ions onto bagasse fly ash (BFA). We use formal model selection criteria to associate each of these four models with a weight, or posterior probability, representing the relative likelihood of each model. When the Kashyap's information criterion (KASHYAP, 1982) is adopted, some of the weights are large enough so that it may not be justified adopting one of the four models at the exclusion of all others.

KEY WORDS: adsorption, geochemistry, ground-water, hydrogeology, precipitation.


PAROLE CHIAVE: acque sotterranee, adsorbimento, geochemica, idrogeologia, precipitazione.
1. - INTRODUCTION

Understanding and modeling reactive transport processes is crucial for the prediction of the complex chemical/physical evolution of Earth systems. Amongst the various reactive transport scenarios which can take place in natural systems, here we focus on the analysis of some aspects associated with (a) precipitation / dissolution reactions in carbonate systems and (b) competitive behavior of heavy metals compounds in soils. Both processes are relevant for the assessment of the quality of the subsurface environment and are characterized by unique conceptual, interpretation and modeling challenges.

Because of their complexity and ubiquity, mixing-driven processes governing the geochemistry of carbonate systems, within which precipitation / dissolution reactions take place, have been extensively studied [e.g., SANFORD & KONIKOW, 1989; SINGURINDY et alii, 2004; REZAEI et alii, 2005, STEEFEL et alii, 2005 and references therein]. The relevance of mixing in these processes is well documented. Mixing occurring at various scales governs chemical speciation in aquatic systems and the distribution of pollutant concentrations in transition regions where surface and subsurface waters interact. It is therefore not surprising that characterization of precipitation / dissolution scenarios relies heavily on the concept of mixing and that major efforts have been devoted to the inclusion of these effects into a series of mathematical formulations. Precipitation / dissolution reactions occurring at interfaces between waters with different chemical compositions lead to modifications in physical-geo-chemical properties of aquifers, such as porosity, hydraulic conductivity and distribution coefficient [SINGURINDY & BERKOWITZ, 2004; REZAEI et alii, 2005; KATZ et alii, 2010]. This has relevant implications in management practices of natural aquifers and reliable approaches are needed to describe changes in macroscale parameters of the groundwater system.

Another problem which is rapidly becoming of pressing concern is the reactive transport scenario associated with the presence of heavy metals in groundwater systems. Heavy metals are a key constituent in a wide variety of industrial and domestic products, processes and applications (including fertilizers, limiting materials, sewage sludge, and compost). Road networks, vehicular emission, housing and emission from municipal waste incinerators are also main sources of metals in urban areas. The subsequent release of these metals to the environment has already caused widespread contamination of soil and water resources. Therefore, heavy metal reactions, in a competitive system, are important to determine heavy metal availability to plants and their mobility throughout the soil. These problems, found worldwide, are especially dramatic in several EU countries. Italy is not immune to this. Critical situations are reported in the northern (e.g., in the sediments of the Lagoon of Venice; see BERNARDELLO et alii (2006)), central (e.g., in urban soils of coastal Tuscany; see BRETZEL & CALDERISI (2006)), and southern (e.g., sites West of the city of Naples; see ADAMO et alii (2002)) regions. Heavy metals, such as chromium, nickel, lead, molybdenum, and vanadium are commonly used in industrial processes that include the production of electronic components, paint, leather tanning, timber processing, and plating of metals, as well as in preparation of many cosmetics and pharmaceuticals. Interconnections between surface waters and groundwater allow heavy metals to migrate into the subsoil and to undergo complex (and mostly unknown) bio-geo-chemical processes in the heterogeneous water-soil system.

The hydro-geo-chemical processes described above involve multiple reactive species and are generally analyzed using advanced numerical codes. Modeling is a challenging problem, necessary for understanding the fate of pollutants and geo-chemical processes occurring in diverse highly heterogeneous environments such as aquifers, rivers, estuaries and oceans. Unfortunately, development of realistic models is complex, both conceptually and mathematically. The governing equations describing reactive transport in porous media are based on (1) conservation of energy, (2) conservation of solid, fluid and solute mass, (3) conservation of momentum (Navier-Stokes equation at the pore scale and Darcy’s Law at some meso- or macro-scale), and (4) constitutive laws for key parameters (including, amongst others, fluid density, viscosity, permeability). The nature of participating species and reactions leads to a broad range of possible different behaviors of the system. These ingredients render the system of governing equations complex and highly non-linear. Basically two types of interpreting approaches can be considered: pore scale and continuum (macroscale) models. If it were possible to model flow and reactive transport at the pore scale over any observation scale of interest (e.g., basin scale) there would be no need to consider other approaches. Unfortunately this is not the case. In groundwater sciences it is practically impossible to solve the Navier-Stokes equations at the pore scale for the problems of common interest (at the laboratory and field scale). Flow and (conservative or reactive) transport phenomena are traditionally described by macroscale
models based on a continuum interpretation of the underlying microscale processes. Since (many) of the physical and chemical processes take place at the pore (and sub-) scales the development of approaches to translate information from this scale to larger scales in essential.

The complete analysis of a reactive transport problem typically involves specification of a large number of aqueous and non-aqueous species. An excellent recent review on the topic is offered by Steefel et alii (2005). Here, we focus only on some recent key modeling aspects. A common method to estimate spatial distributions of chemical species concentrations and associated reaction rates is to resort to numerical modeling. A series of mathematical formulations are available in the literature (e.g., Rubin, 1990; Yeh & Tripathi, 1991; Friedly & Rubin, 1992; Rubin, 1992; Lichtner, 1996; Steefel & Mac Quarrie, 1996; Clement et alii, 1998; Saaltink et alii, 1998, 2001; Tebes-Stevens et alii, 1998; Robinson et alii, 2000; Molins et alii, 2004), which are included in a variety of codes. All these methodologies are based on the idea that the reactive transport problem can be reformulated in terms of a subset of conservative transport scenarios. The methodology typically consists of the following steps: (a) defining conservative components, which are usually linear combinations of reactive species concentrations, and decouple the solution of the equations associated with the chemical reactions from the mass balance of chemical compounds; (b) solving the transport equations for the conservative components by means of standard Eulerian or Lagrangian methods; (c) performing speciation calculations to obtain the concentration of aqueous species from the space-time distribution of components; and (d) substituting the latter into the transport equations to evaluate numerically reaction rates. This approach is appealing for its simplicity and can be applied when the concentrations of the reacting species stand in algebraic relationship to each other, the coefficients describing physical mixing in the system coincide for all compounds, and all aqueous species are advected by the same (meso-scale) velocity. The first requirement is met by systems either in local chemical equilibrium or instantaneous, complete, irreversible reactions (e.g., Liedl et alii, 2005) and can also be used for specific cases of kinetic reactions (Girpka & Valocchi, 2007; Molins et alii, 2004).

A methodology to compute directly homogeneous and heterogeneous reaction rates under instantaneous equilibrium has been presented recently by De Simoni et alii (2005, 2007). It allows to calculate the rate of the reactions as a function of quantities such as the concentration of components, the equilibrium constants, and the dispersion coefficients, without the need to calculate the concentration of the dissolved species. The results of De Simoni et alii (2007) suggest that the problem of assessing reaction rates in a reactive system involving a relatively high number of aqueous and constant activity species can be decoupled into a transport problem posed in terms of mixing ratios plus a speciation term. Their general expression for the reaction rates illustrates that mixing processes control equilibrium reaction rates. The methodology has then been extended (Sánchez-Vila et alii, 2010) to include a scenario where the geo-chemical system can be described by an arbitrary number of equilibrium (fast) reactions and one kinetic (slow) reaction, in the absence of non-constant activity immobile species. As compared to formulations proposed previously in the literature (e.g., Molins et alii, 2004; Rubin, 1990, 1992; Saaltink et alii, 1998, 2001), this method is simpler and more concise and conducive to an analytical expression for the reaction rates that includes the model of Phillips (1991) as a particular case. In essence, it allows the direct evaluation of the distribution of reaction rates of a complex multispecies reactive transport problem by solving two independent problems: (a) the transport of one or more conservative species, and (b) chemical speciation. The method can only be applied when the mineral is present for all mixing ratios, which can not always be the case. While in general the calculation of the reaction rates is performed numerically, in some cases, typically in the context of uniform systems in the presence of uniform seepage flow and specific types of solute injection, it is possible to obtain closed-form analytical solutions (De Simoni et alii, 2005, 2007). The approach has been used by Guadagnini et alii (2008) in conjunction with laboratory-scale CaCO3 dissolution experiments reported in Singurindy et alii (2004, 2005) to describe the spatial distribution of reaction rates in a homogeneous flow cell.

A number of recent observations and findings show that multicomponent reactive transport behavior and its link to the geo-chemical properties of the aquifer and to the phenomena involved at the pore scales are far from being completely understood. For example, De Simoni et alii (2005) analyzed the spatial distribution of the total precipitation rate for a typical precipitation/dissolution problem. The authors observed that the location of the center of the plume does not coincide with the position of the maximum precipitation rate. Katz et alii (2010) performed conservative
and reactive transport experiments in a quasi-two-dimensional laboratory flow cell, filled with homogeneous and heterogeneous porous media. Conservative experiments were performed by injecting solutions containing sodium chloride and calcium chloride into the domain. In reactive transport experiments, inlet solutions of calcium chloride and sodium carbonate were injected in parallel. The reactive transport experiments featured the formation of a calcium carbonate mineral phase within the mixing zone between the two solutions, which controlled the spatial evolution of calcium carbonate in the domain. Numerical simulations performed on high resolution grids for both the homogeneous and heterogeneous porous systems underestimated clogging of the system. Although qualitative agreement between model results and experimental observations was obtained, accurate model predictions of the spatial evolution of calcium concentrations at sample points within the flow cell could not be achieved. Phenomena such as chelation and simultaneous presence of several metals add to the list.

Notwithstanding the above concerns and research efforts, only over the last years has the impact of competitive behavior of heavy metals in solute transport been recognized (e.g., MAYES et alii, 2000; GOMES et alii, 2001; SAHA et alii, 2002; FONTES & GOMES, 2003; SRIVASTAVA et alii, 2005). Most of the studies that analyze the problem of metal competition are performed under batch conditions. SAHA et alii (2002) found that the competition between Cd and Zn increases with the initial concentration of the metals on Montmorillonite (Mt), Hydroxyaluminium-Mt (HyA-Mt) and Hydroxyaluminiosilicate-Mt (HAS-Mt). When the initial concentration is less than 5 × 10^{-5} M, the addition of a second metal has little effect on the adsorption of a given metal, which suggests that each metal preferentially binds to different sites (i.e., their preferred binding sites do not overlap each other). Similarly, FONTES & GOMES (2003) found that, in soils of tropical and sub-tropical area (Oxisols, Ultisols, Alfisols) heavy metals (Ni, Zn, Cd, Cr, Cu, Pb) are adsorbed proportional to their relative molar concentration at the lowest concentration applied in their experiments. As the concentration increases, competition starts to occur and the proportion of the stronger competitors (Cr, Cu, Pb) increases, as compared with the weakest ones (Ni, Zn, Cd). SRIVASTAVA et alii (2005) considered the competitive adsorption of heavy metals on kaolinite for varying pH conditions. The adsorption behavior of Cd, Cu, Pb and Zn in single- and multi-element system differs. The selectivity sequence is Cu > Pb > Zn > Cd in a single element system and Pb > Cu > Zn > Cd in a multi-element system. These results can be relevant to the analysis of the potential of strongly contaminated soils to adsorb and retain heavy metals during groundwater remediation activities. In addition to batch experiments, only a limited set of flow-through experiments has been performed (e.g., VÖEGELING et alii, 2001; CHANG et alii, 2001; TSANG & LO, 2006; ANTONIADIS et alii, 2007). The Freundlich model has been found to describe monometal sorption satisfactorily. Various alternative models have been proposed to predict metal sorption in competitive systems. These include (a) a modification of the Freundlich model introduced by SHEINDORF et alii (1981), referred to as the SRS model, (b) a modified competitive Langmuir isotherm (BELLOT & CONDORET, 1993), and (c) and extended Langmuir model (YANG, 1987). Examining the applicability of existing multi-component adsorption isotherm equations to the competitive adsorption equilibria of the metals in a multi-component system is still an open problem.

Following the brief literature review presented, our aim is to present some aspects associated with the interpretation of reactive multi-component transport in porous media. In Section 2 we start by illustrating the main theoretical aspects underlying the general formulation of a reactive transport problem. For ease of discussion, we focus on equilibrium reactions. Section 3 describes some of the key results obtained by GUADAGINI et alii (2009), who presents a modeling study of the dissolution laboratory-scale experiments performed by SINGURINDY et alii (2004, 2005). Finally, Section 4 presents a comparative analysis of the ability of some alternative models to interpret the competitive bi-metal sorption batch experiments presented by SRIVASTAVA et alii (2006).

2. - THEORETICAL BASIS

Modeling reactive transport involves describing mass balances of species and reactions among species. The basic equations, an ADRE (Advective-Dispersive-REactive) formulation, and the strategy adopted to solve them, are described below.

2.1. - SPECIES TRANSPORT EQUATIONS

A species mass balance can be written as

\[
\frac{\partial (\mathbf{m})}{\partial t} = \mathbf{M} \mathbf{z} (\mathbf{e}) + \mathbf{f}
\]  

(1)
Here, vector \( \mathbf{m} \) contains the moles of species per unit volume of porous medium and vector \( \mathbf{c} \) contains species concentrations in mol/mass of liquid \( (m_f = \mathbf{P}\mathbf{C}_i \text{ for the } i\text{-th mobile species in a system of porosity } \phi \text{ and liquid density } \rho ) \). Matrix \( \mathbf{M} \) is diagonal and its diagonal terms are unity when a species is mobile and zero otherwise; \( \mathbf{f} \) is a source/sink term, which we use to represent chemical reactions. Here we define the linear operator \( L(\mathbf{r}) \) in (1) as \( L(\mathbf{r}) = -\mathbf{D} \cdot (\mathbf{r} \mathbf{v}) + \mathbf{v} \cdot (\mathbf{D} \mathbf{v}) \), where \( \mathbf{D} \) is the diffusion/dispersion tensor and \( \mathbf{v} \) is the fluid velocity, \( \mathbf{v} = q/\phi, q \) being Darcy’s flux vector. In the application presented in Section 3, we assume that all mobile species are characterized by the same coefficients depicting physical mixing, along the lines of, e.g., SAALTINK et alii (1998) and MOLINS et alii (2004). This condition requires that hydrodynamic dispersion dominates over pore-scale diffusion in the relevant mixing process.

2.2. - EQUILIBRIUM REACTIONS

Reactions can be considered at equilibrium when the time scales involved in the various chemical reactions occurring in the system are small with respect to typical diffusive and advective time scales. In our application we only consider aqueous reactions and precipitation-dissolution of minerals. We define \( \mathbf{f} = \mathbf{S}_e \mathbf{r} \), where \( \mathbf{r} \) is the vector of reaction rates (expressed per unit volume of porous medium) and \( \mathbf{S}_e \) contains species concentrations in mol/mass of source/sink term, which we use to represent chemical reactions. Following DE SIMONI et alii (2005, 2007), we define \( \mathbf{U} \) so that \( \mathbf{S}_{e}^{\text{aq}} = (\mathbf{S}_e, \mathbf{0})^T \).

Multiplying (1) by \( \mathbf{U} \) leads to

\[
\frac{\partial (\mathbf{m})}{\partial t} = -\mathbf{L} (\mathbf{m}) + \mathbf{S}_e \mathbf{r},
\]

where vector \( \mathbf{m} \) contains the mass of constant activity species and \( \mathbf{u} \) is a vector of \( N_e \) (aqueous) components defined as

\[
\mathbf{u} = \mathbf{u}_c = \mathbf{c}_e + (\mathbf{S}_e^{\text{aq}})^T \mathbf{c}_a.
\]

Equation (6) represents \( N_e \) transport equations. Vector \( \mathbf{u} \) contains only aqueous species so that we can leave out matrix \( \mathbf{M} \) in (6), while \( \mathbf{M}_c \) in (5) is the part of \( \mathbf{M} \) referring to constant activity species. As \( \mathbf{S}_e^{\text{aq}} \) may vary in time and space, \( N_e \), \( N_a \) and matrix \( \mathbf{U} \) may vary as well.

If the definition of the chemical system does not change, the easiest way to solve (6) is to first solve \( \mathbf{u} \) (with appropriate boundary and initial
conditions. Then, (aqueous) solute concentrations are obtained from the expression of \( \mathbf{u} \) in terms of concentrations of species (7) and the mass action law (2). Equilibrium reaction rates are then calculated, \( \mathbf{c}_\sigma \), from transport equations (1) of secondary species as

\[
r = i \{ \mathbf{c}_\sigma \} - \frac{\partial (\mathbf{c}_\sigma \mathbf{b})}{\partial \mathbf{x}}.
\]

The mass evolution of the constant activity species is finally obtained upon substituting \( \mathbf{r} \) into (5).

2.4. - MODIFICATION OF MEDIUM PROPERTIES

Dissolution/precipitation processes may lead to changes in medium properties, specifically porosity and hydraulic conductivity, which have a major influence on groundwater velocity. To assess the importance of these effects, porosity variability needs to be included in the numerical simulations of experiments. Permeability \( \mathbf{k} \) updating can be performed for each time step on the basis of, e.g., the Kozeny relationship

\[
k = k_0 \left( \frac{\phi}{1 - \phi} \right)^3
\]

where \( k_0 \) and \( \phi_0 \) denote initial permeability and initial porosity, respectively. The porosity is calculated from the concentrations of minerals as

\[
\frac{\partial \phi}{\partial \mathbf{x}} = \sum_m \phi_m \frac{2 \rho_m}{\rho}
\]

where subscript \( m \) refers to a mineral and \( \rho \) is the molar volume.

2.5. - ANALYTICAL EXPRESSION OF REACTION RATES

The analyses presented above clearly shows that \( \mathbf{c}_\sigma \) is a function of the space-time distribution of components, \( \mathbf{u} \), as well as chemical equilibrium constants, i.e., \( \mathbf{c}_\sigma = f(\mathbf{u}, K) \), where \( f() \) represents a functional relationship described on the basis of (2) and (7). DE SIMONI et alii (2005) derived a general analytical expression rendering the space-time distribution of reaction rates. When chemical equilibrium parameters are uniform in space and time, the rate of the \( m \)-th reaction is given by the following expression (DE SIMONI et alii, 2005) where, for simplicity, we did not adopt a vectorial notation

\[
\mathbf{z}_i = \phi \rho \sum_m \frac{\partial \mathbf{c}_m}{\partial \mathbf{x}} \nabla \mathbf{u} \nabla \mathbf{u}_i.
\]

DE SIMONI et alii [2007] have extended (11), developing a formulation which provides reaction rates in terms of the mixing ratios of waters with different chemical signatures in the presence of precipitation / dissolution reactions under equilibrium conditions. In this context, one starts by identifying the different waters taking part in the observed processes. A vector of mixing ratios, \( \mathbf{\beta} = (\beta_1, ..., \beta_N) \), is then introduced. Here, \( \beta_i \) is the volumetric proportion of the \( i \)-th (\( i = 1, ..., N \)) water in a sample. Mixing of \( N \) waters originates \( (N - 1) \) independent variables as mixing ratios sum up to unity. Mixing ratios are conservative quantities, the evolution of which is described by nonreactive transport equations

\[
\frac{\partial \mathbf{c}_m}{\partial \mathbf{x}} = i \{ \mathbf{c}_m \}
\]

with given initial and boundary conditions. DE SIMONI et alii (2007) derived the following formulation, expressing reaction rates in terms of mixing ratios

\[
r = \mathbf{\beta} \nabla \mathbf{c}_m \left( \nabla \mathbf{\beta} \mathbf{D} \nabla \mathbf{\beta} \right)
\]

On these bases, it is clear that reaction rates can be calculated directly, without the need to solve the complete reactive transport problem. Several alternatives are available to compute the first term appearing on the RHS of (13). In simple cases, \( \mathbf{\partial} \mathbf{c}_m / \partial \mathbf{\beta} (\mathbf{c}_m) \) is the concentration of the \( m \)-th secondary species can be evaluated analytically or numerically. In general, chemical speciation routines capable of providing the functional dependence of \( \mathbf{c}_m \) on \( \mathbf{\beta} \) are a standard option of codes such as PHREEQC (PAKHURST & APPELO, 1999), RETRAYO (SAALTINK et alii, 2004), or CHEPROO (BEA et alii, 2009).

3. - MODELING OF LABORATORY-SCALE DISSOLUTION EXPERIMENTS

Here we present the main results obtained by applying the modeling techniques illustrated in Section 2 to analyze CaCO3 dissolution experiments performed in a homogeneous laboratory flow cell and presented by SINGURINDY et alii (2004, 2005). The experiments are modeled on the basis of (a) the numerical solution of the complete system of equations describing the reactive transport problem and (b) the decoupled methodology of DE SIMONI et alii (2005, 2007), which allows calculating directly the rate of the reactions occurring in the system.

3.1. - SYNTHETIC DESCRIPTION OF THE EXPERIMENTS

The experimental set-up described in SINGURINDY et alii (2004, 2005) consisted of a \( 16 \times 16 \times 1 \text{ cm}^3 \) flow cell packed with CaCO3 particles, to produce a uniform porous system. The cell was connected to two inlet reservoirs: one containing 40 g/L NaCl dissolved in double
deionized water (hereafter called “saltwater”) and the other containing only double deionized water (“freshwater”). Before injection into the cell, both waters were brought into contact with calcite and with CO₂ at a partial pressure of 1 atm until conditions of chemical equilibrium were obtained. Further details regarding the set-up are reported by Singurindy et alii (2004). The dissolution experiments we consider differ from each other in terms of the ratio between fresh and saltwater flow inlet rates, the total volumetric flow rate, \(Q\), comprising both fresh water and salt water, being the same in all three experiments (\(Q=1.44 \times 10^{-3}\) m³ day⁻¹). On the basis of measurements of cumulative differences between inlet and outlet Ca²⁺ concentrations, Singurindy et alii (2004, 2005) calculated a global dissolution rate for the system. Key data and experimental results are reported in table 1. Experimental results are associated with a pseudo-steady state condition, in which aqueous species concentrations do not vary in time while mineral (CaCO₃) concentrations do. This condition is frequently used in the analysis of the evolution of carbonate systems in coastal aquifers (e.g., Sanford & Konikow, 1989; Rezaei et alii, 2005).

3.2. - Modeling approach based on the solution of the full geochemical system

We start by using the code PHREEQC (Pakhurst & Appelo, 1999) to calculate the chemical composition of the two inflowing waters used in the experiments under the assumption of equilibrium with respect to calcite and a partial CO₂(g) pressure of 1 atm. PHREEQC also provides the relevant aqueous complexation reactions. The complete chemical system is formed by 19 chemical species and 13 reactions. All reactions and their equilibrium constants are displayed in table 2. The flow and reactive transport problem is modeled with the numerical code RETRASO (Saaltink et alii, 2004), following the methodology illustrated in Section 2. The complete numerical solution of the reactive transport problem entails: (a) solving 4 conservative ADEs, (b) performing speciation calculations, consisting in the solution of a nonlinear system of 17 algebraic equations, and finally (c) calculating numerically the reaction rates by solving the 13 transport

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log (K_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl⁺ = Ca²⁺ + Cl⁻</td>
<td>0.6938</td>
</tr>
<tr>
<td>CaCl₂(aq) = Ca²⁺ + 2Cl⁻</td>
<td>0.6283</td>
</tr>
<tr>
<td>CaHCO₃⁺ = Ca²⁺ + HCO₃⁻</td>
<td>-1.0606</td>
</tr>
<tr>
<td>CaOH⁺ + H⁺ = Ca²⁺ + H₂O</td>
<td>12.9321</td>
</tr>
<tr>
<td>CO₂(aq) + H₂O = HCO₃⁻ + H⁺</td>
<td>-6.3636</td>
</tr>
<tr>
<td>CO₃²⁻ + H⁺ = HCO₃⁻</td>
<td>10.3524</td>
</tr>
<tr>
<td>OH⁻ + H⁺ = H₂O</td>
<td>14.0707</td>
</tr>
<tr>
<td>HCl(aq) = H⁺ + Cl⁻</td>
<td>0.6693</td>
</tr>
<tr>
<td>NaCl(aq) = Na⁺ + Cl⁻</td>
<td>0.7811</td>
</tr>
<tr>
<td>NaCO₃⁻ + H⁺ = Na⁺ + HCO₃⁻</td>
<td>9.8145</td>
</tr>
<tr>
<td>NaHCO₃(aq) = Na⁺ + HCO₃⁻</td>
<td>-0.1715</td>
</tr>
<tr>
<td>NaOH(aq) + H⁺ = Na⁺ + H₂O</td>
<td>14.2479</td>
</tr>
<tr>
<td>CaCO₃(s) + H⁺ = Ca²⁺ + HCO₃⁻</td>
<td>1.8789</td>
</tr>
</tbody>
</table>
equations with the format of (1) satisfied by the secondary species. Steady-state flow within a homogeneous, two-dimensional porous domain is modeled. A uniform intrinsic permeability of \( k = 3.975 \times 10^{-10} \text{ m}^2 \) (Singrindy & Berkowitz, 2003) was adopted. Inflow boundaries are modeled by imposing a constant volumetric flux, uniformly distributed along the inlet boundaries according to the data presented in table 1.

A constant head equivalent to atmospheric pressure is imposed at the outflow boundaries. Porosity, \( \phi \), was set to the measured value of 0.33 (Singrindy et alii, 2004). Transport parameters, \( i.e. \), dispersivities, are calibrated for the experiments by comparing the calculated total rates to experimental rates (reported in table 1). The latter are derived on the basis of the available experimental data, which consist of the overall dissolved calcite concentrations, \( C_{\text{CaCO}_3} \), evaluated at times \( t \), and computed by mass balance from the inflow and outflow \( \text{Ca}^2+ \) concentrations. The domain was discretized into square finite elements of uniform size \( \Delta = 0.133 \text{ cm} \), \( i.e. \), 120 \( \times \) 120 elements. For simplicity, and due to lack of sensitivity of the model results to longitudinal dispersivity, \( \alpha_L \), the diffusion-dispersion process has been modeled as isotropic, and we set \( \alpha_L = \alpha_L = \alpha \) as the only fitting parameter. The calibration procedure to match the experiments resulted in the following values of dispersivities: (a) \( \alpha = 0.0010 \text{ m} \) for the 50/50 experiment (Experiment 1 in table 1); and (b) \( \alpha = 0.0040 \text{ m} \) for the 70/30 experiment (Experiment 3 in table 1). Due to software constraints, it was not possible to adopt a grid refinement compatible with very low dispersivity values which would have been needed in order to obtain a good calibration of the 30/70 experiment (Experiment 2 in table 1). We note that the isotropic dispersivity providing the best agreement against experimental results tends to decrease as the proportion of salt water increases. Factors which might contribute to this behavior include sensitivity of the model to the chemical composition of the inlet waters, and temperature effects that could influence the activity coefficients.

3.3. - MODELING APPROACH BASED ON THE DIRECT CALCULATION OF LOCAL REACTION RATES

Since only two end-members are present, the chemical problem is characterized completely by a single mixing ratio, \( \beta \). Assuming that solute transport can be properly described by means of an advection-dispersion (or advection-diffusion) equation, De Simoni et alii (2007) provided an explicit expression for the computation of local reaction rates \( r \) in terms of \( \beta \).

\[
\frac{r}{\phi} = \frac{\partial}{\partial t} \frac{c_{\text{Ca}}}{\phi} \sqrt{\beta} \nabla \nabla \beta \quad (14)
\]

where \( r \) is expressed in \( \text{mol kg}^{-1} \text{s}^{-1} \). Here, \( c_{\text{Ca}} \) in (15) corresponds to total aqueous concentration of calcium. Mixing ratios, \( \beta \), can be obtained from any conventional transport or random walk particle tracking code. The nonlinear chemistry-related factor, \( A_i \), in (14) can be calculated by plotting the total aqueous calcium concentration, \( c_{\text{Ca}} \), versus mixing ratio, \( \beta \), for a suite of arbitrary mixing scenarios. To this end, an existing speciation codes, such as PHREEQC, can be used. We calculate the local distribution of rates under pseudo-steady-state transport conditions at constant temperature according to (14), and then integrate it over the flow cell volume to obtain the total reaction rate within the system. Dispersivities are then calibrated for each of the three experiments by comparing the calculated total rates to experimental rates (reported in table 1). Dispersivities values providing the best match between experimental and computed global reaction rates coincide with those obtained by means of the fully numerical geochemical modeling approach for the 50/50 and 70/30 experiments. A good calibration of the 30/70 experiment against numerical modeling results was obtained by adopting the isotropic dispersivity value \( \alpha = 0.0002 \text{ m} \). It is remarked that the calibrated (isotropic) dispersivity values are of the order of the pore size of the porous rock, thus being (in principle) suitable for describing mixing at the molecular scale. Although all calibrated values are within an order of magnitude, the variability in the values cannot be explained solely on the basis of error measurements and uncertainty. This may be due to the use of an ADRE-based continuum model in the presence of pore-scale reactions. As noted by Tartakovsky et alii (2008, and references therein) and further discussed by Katz et alii (2010), several scale separation conditions must be maintained (e.g., the characteristic length associated with the pore space separation must be much smaller than the characteristic length of the averaging volume) to allow use of the ADRE. These conditions are often violated in transport processes that involve mixing, and might contribute to explain the results obtained.

4. - MODELING OF LABORATORY-SCALE COMPETITIVE ADSORPTION EXPERIMENTS

This Section is devoted to the interpretation of the competitive adsorption of cadmium (Cd(II)) and nickel (Ni(II)) ions onto bagasse fly ash (BFA) performed by Srivastava et alii (2006).
4.1. - OVERVIEW OF THE EXPERIMENTS

SRIVASTAVA et alii (2006), performed a series of batch experiments involving mono- and binary-component adsorption studies of cadmium (Cd(II)) and nickel (Ni(II)) ions onto bagasse fly ash (BFA). Experimental details on the preparation and characterization of the BFA samples, the chemical composition of the solutions adopted in the experiments, and the protocols adopted to measure Cd(II) and Ni(II) concentrations are presented by SRIVASTAVA et alii (2006). For single metal systems, initial metal ion concentration was varied from 10 to 100 mg/l. In binary metal ion mixtures, for each initial concentration of Cd(II) solution, i.e., 10, 20, 30, 50 and 100 mg/l, the nickel concentration was varied in the range of 10–100 mg/l (i.e., 10, 20, 30, 50 and 100 mg/l). In all cases, the pH of the solution was maintained at 6.0. Experiments were carried out until equilibrium conditions were attained. The complete data-set of 50 individual and total adsorption equilibrium uptakes and yields were carried until equilibrium conditions were attained. The complete data-set of 50 individual and total adsorption equilibrium uptakes and yields were attained. The complete data-set of 50 individual and total adsorption equilibrium uptakes and yields were attained. The complete data-set of 50 individual and total adsorption equilibrium uptakes and yields were attained.

Single-component isotherms have been modeled by Freundlich, Langmuir and R-P models. Bi-component isotherms were interpreted by several models. These include the Sheindorf–Rebuhn–Sheintuch (SRS) model (SHEINDORF et alii, 1981)

\[ q_{e1} = K_{r1} C_{e1} \left( \sum_{i=2}^{N} q_{e1} C_{e1} \right)^{y1} \] (15)

the modified competitive Langmuir isotherm (BELLOT & CONDORET, 1993)

\[ q_{e1} = \frac{K_{r1} C_{e1} \eta_1}{1 + \sum_{i=2}^{N} \eta_i} \] (16)

the extended Langmuir isotherm (YANG, 1987)

\[ q_{e1} = \frac{\sum_{i=1}^{N} K_i C_{e1}}{1 + \sum_{i=1}^{N} K_j C_{e1}} \] (17)

and the extended Freundlich model

\[ q_{e1} = \frac{K_{r1} C_{e1}^{1+y1}}{C_{e1}^{1+y1} + y1 C_{e1}^{1+y1}} \] \[ q_{e2} = \frac{K_{r2} C_{e2}^{1+y2}}{C_{e2}^{1+y2} + y2 C_{e2}^{1+y2}} \] (18)

Here, \( N \) is the number of metals involved in the competitive experiment (in our case \( N = 2 \)); \( q_{e1,j} \) and \( K_{p1} \) are the parameters of the individual Langmuir isotherm models; \( K_{r1,j} \) and \( \eta_1 \) are the Freundlich parameters determined from the single-component equilibrium adsorption data; the isotherm parameters \( \eta_1, q_{m1}, K_{p1}, N_1, j_1, z_1, N_2, j_2, z_2 \) and \( \eta_j \) are determined using a best-fit procedure against the experimental data. SRIVASTAVA et alii (2006) assessed the quality of the fit of the different models analyzed on the basis of the minimized Marquardt’s percent standard deviation. On these bases, they conclude that the binary adsorption of Cd(II) and Ni(II) ions by BFA can be represented satisfactorily and adequately by the extended Freundlich isotherm (18).

4.2. - INTERPRETATION BASED ON MULTIMODEL APPROACH

Hydrogeochemical processes taking place in complex subsurface environments are prone to multiple interpretation and mathematical descriptions. As a consequence, adopting only one of these might lead to statistical bias and underestimation of uncertainty. In the spirit of NEUMAN (2003) we adopt formal model selection (discrimination, information) criteria to select the best amongst the different competing models (15) - (18). We associate each of these four models with a weight, or posterior probability, representing their relative degrees of likelihood.

Let \( \beta \) be a vector of unknown model parameters. We wish to obtain a maximum likelihood (ML) estimate \( \hat{\beta} \) of \( \beta \) based on \( N \) measurements of adsorbed ions concentration at equilibrium, \( q_{e1,j}^*, q_{e2,j}^* \),

\[ q_{e1,j}^* = q_{e1,j} + e_{j1}^*, \quad q_{e2,j}^* = q_{e2,j} + e_{j2}^* \] \( j = 1, 2, ..., N \) (19)

where \( q_{e1,j} \) is the unknown true value of adsorbed ion concentration corresponding to given values of initial \( (C_{0}) \) and equilibrium \( (C_{e1}) \) concentrations and \( j^* \) is a corresponding zero-mean measurement error. We designate the vectors of adsorbed ion concentration measurements and corresponding measurement errors by \( \mathbf{q}^* \) and \( \mathbf{e}^* \), respectively. Following the rationale of CARRERA & NEUMAN (1986a,b) we treat the prior error vectors as being multivariate Gaussian, an assumption that can be validated a posteriori by a statistical analysis of the corresponding residuals \( \mathbf{e}^* = \mathbf{q}^* - \mathbf{q}^* \), \( \mathbf{q}^* \) being a vector of adsorbed ion concentrations predicted using parameter estimates \( \hat{\beta} \). For simplicity and without loss of generality, we assume that measurement error statistics lack correlation. Then a ML estimate of \( \hat{\beta} \) is obtained by minimizing the negative log likelihood function (support function)

\[ NLL = \left( N + N_p \right) \ln(2\pi) + \ln | \mathbf{S}_q \| + \left( \mathbf{q}^* - \mathbf{q}^* \right)^T \mathbf{S}_q^{-1} \left( \mathbf{q}^* - \mathbf{q}^* \right) \] (20)

with respect to \( \beta \). Here, \( N_p \) is the number of model parameters, \( \mathbf{S}_q = \sigma_q^2 \mathbf{V}_q^T \) is a diagonal covariance matrix of measurement errors, \( \mathbf{e}^* \), where \( \mathbf{V}_q \) is the identify matrix and is determined upon minimizing of (20) though it may have an estimated prior value. If the prior estimate of \( \sigma_q^2 \) is considered reliable and is fixed, then the minimization of (20) reduces to minimization of the generalized
sum of squares criterion. We minimize (20) using the iterative Levenberg-Marquardt algorithm implemented in the public domain code PEST (Doherty, 2002). The minimization algorithm computes an updated parameter estimate \( \tilde{\mathbf{q}} \) of the (unknown) true vector \( \mathbf{q} \) and a Cramer-Rao lower bound approximation for the covariance matrix, \( \mathbf{Q} \), of the corresponding estimation errors; the latter is evaluated according to

\[
\mathbf{Q} = \sigma^2_{\mathbf{D}} \mathbf{J}^T \mathbf{V}_{\mathbf{f}}^{-1} \mathbf{J}
\]

where \( \mathbf{J} \) is a Jacobian matrix of derivatives of the adsorbed ion concentrations with respect to \( \mathbf{B} \), evaluated at \( \mathbf{B} \). We repeat the parameter estimation procedure for each of the interpretive models described in Section 4.1 and then we select an optimum model based on how sharply it corresponds to a minimum of any of the following model selection (discrimination, information) criteria

\[
AIC = N \log L + 2N_p
\]

(21)

\[
AIC_c = N \log L + 2N_p \frac{N_p + 2}{N - 1}
\]

(22)

\[
BIC = N \log L + N_p \log(N + N_p)
\]

(23)

\[
HIC = N \log L + 2N_p \log(N + N_p)
\]

(24)

\[
KIC = N \log L + N_p \log(N + N_p) - \frac{1}{2} \log |\mathbf{Q}|
\]

(25)

\( AIC \) is due to Akaike (1974), \( AIC_c \) to Hurvich & Tsai (1989), \( HIC \) to Hannan (1980), \( BIC \) to Schwartz (1978), and \( KIC \) to Kashyap (1982).

Following Ye et alii (2004) we translate the values of (21) - (25) into posterior model weights for model \( M_k \) (in our case, we have \( k = 4 \) alternative models), \( p(M_k | \mathbf{q}) \), which represent posterior model probability conditioned on the vector \( \mathbf{q} \) of measures. We compute posterior model weights using an approach proposed by Tsai & Li (2008) according to which

\[
p(M_k | \mathbf{q}) = \frac{\exp\left(-\frac{1}{2} \alpha \Delta IC_k\right)}{\sum_k \exp\left(-\frac{1}{2} \alpha \Delta IC_k\right)} p(M_k)
\]

(26)

where \( \Delta IC_k \) is the difference between the model information criterion \( IC \) (it can be \( AIC, AIC_c, BIC, HIC \) or \( KIC \)) of model \( k \) and the minimum value of the model selection criterion over all the 4 models, \( p(M) \) is the prior model probability (which we take to be equal for all models, i.e., \( p(M) = 1/4 \)) and

\[
\alpha = \frac{s_1}{s_2 \sigma^2_D}
\]

(27)

is a scaling factor. In (27), \( s_1 \) is \( \Delta IC_k \) corresponding to a given significance level in Occam’s window and \( s_2 \) is the width of a variance window, in units of \( \sigma^2_D \), where \( \sigma^2_D = 2N \) is the variance of \( IC_k \). A significance level of 5% corresponds to \( s_1 = 6 \) and a window size of \( 4\sigma^2_D \), i.e., \( s_2 = 4 \) and thus \( \alpha = 0.15 \).

Table 3 lists the values of the selection criteria (21) - (25) associated with each of the models (15) - (18), together with the corresponding model weights. All five criteria in Table 3 rank the extended Freundlich model (18) as best, the SRS model (15) as second best, the modified competitive Langmuir (16) as third, the extended Langmuir isotherm (17) as worst among these four models.

### Table 3 - Values of the selection criteria (12)-(25) associated with each of the models (15) - (18). The corresponding model weights are reported in parenthesis.

<table>
<thead>
<tr>
<th>Eq. (15)</th>
<th>Eq. (16)</th>
<th>Eq. (17)</th>
<th>Eq. (18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIC</td>
<td>40.02 (0.022)</td>
<td>54.72 (0.007)</td>
<td>58.47 (0.005)</td>
</tr>
<tr>
<td>AICc</td>
<td>40.34 (0.025)</td>
<td>55.05 (0.008)</td>
<td>59.08 (0.006)</td>
</tr>
<tr>
<td>BIC</td>
<td>43.92 (0.039)</td>
<td>58.62 (0.013)</td>
<td>64.38 (0.009)</td>
</tr>
<tr>
<td>HIC</td>
<td>41.51 (0.028)</td>
<td>56.23 (0.009)</td>
<td>60.74 (0.007)</td>
</tr>
<tr>
<td>KIC</td>
<td>45.25 (0.021)</td>
<td>62.85 (0.056)</td>
<td>82.31 (0.013)</td>
</tr>
</tbody>
</table>

\( AIC, AIC_c, BIC, \) and \( HIC \) assign a weight of about 96% to the extended Freundlich model (18). \( KIC \) assigns a weight of about 73% to (18), 20% to (15) and virtually 0% to (16) and (17). We note that Kashyap's criterion favors the model that is least probable (in an average sense) of being incorrect. Stated otherwise, the criterion minimizes the average probability of selecting the wrong model among a set of alternatives. The Fisher information term, which is proportional to \( \mathbf{Q} \), imbues \( KIC \) with desirable model selection properties not shared by other criteria, such as \( BIC \), as it has the ability to discriminate between models on the basis not only on their goodness-of-fit to available observations and number of parameters but also on the quality of the available data and of the parameter estimates. According to \( KIC \), the results of table 3 imply that whereas models based on (16) and (17) can validly be eliminated as being inferior to the other two models, there is no justification for adopting any one of the latter two models (the extended Freundlich (18) and the SRS model (15)) at the exclusion of the remaining one. Instead, there is uncertainty about each of these two models and their parameters. A possibility to account for this uncer-
tainty is to average predictions of competitive adsorption of Cd(II) and Ni(II) ions by BFA rendered by (15) and (18) using the weights in Table 3, and to assess the corresponding predictive uncertainty accordingly, using, e.g., maximum likelihood Bayesian model averaging (MLBMA) as described in Neuman (2003), Ye et alii (2004, 2008) and Tsai & Li (2008).

5. - CONCLUSIONS

We have presented a synthetic review of recent modeling developments associated with the interpretation of reactive transport problems. We then present the salient results of modeling studies of (a) dissolution experiments performed in a laboratory-scale porous medium, and (b) binary-component adsorption analyses of cadmium and nickel ions onto bagasse fly ash (BFA). Our work highlights the following key conclusions.

As shown by Guadagnini et alii (2009), it is possible to use a simple methodology of the kind recently presented by De Simoni et alii (2005, 2007) to interpret relatively complex dissolution processes at the laboratory scale.

The performance of four popular models describing heavy metals competition in batch experiments has been analyzed against a set of published data. With the aid of formal model selection criteria we associate each of these four models with a weight, or posterior probability, representing their relative degrees of likelihood. When the Kashyap’s information criterion (Kashyap, 1982) is adopted, some of the weights are large enough so that it may not be justified adopting one of the four models at the exclusion of all others. This suggests that predictions of competitive adsorption of Cd(II) and Ni(II) ions by BFA can be best performed in the context of a multimodel approach, such as maximum likelihood Bayesian model averaging.

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