

## CÓDIGOS COMPUTACIONAIS DE MODELAGEM GEOQUÍMICA UTILIZADOS PARA INTERAÇÃO ÁGUA-ROCHA EM SISTEMAS SIMPLES E COMPLEXOS

## COMPUTER CODES OF GEOCHEMICAL MODELING USED TO WATER-ROCK INTERACTION SIMPLE AND COMPLEX SYSTEMS

KLUNK, Marcos Antônio<sup>1\*</sup>; DASGUPTA, Sudipta<sup>2</sup>; DAS, Mohuli<sup>2</sup>; WANDER, Paulo Roberto<sup>1</sup><sup>1</sup> University of Vale do Rio dos Sinos, Graduation Program in Mechanical Engineering<sup>2</sup> Department of Earth Sciences, IIT Bombay, India Federation

\* Correspondence author  
e-mail: marcosak@edu.unisinos.br

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## RESUMO

A modelagem numérica de transporte e reação foi utilizada para o entendimento da evolução dos processos diagenéticos e sua importância na caracterização e previsão da qualidade dos reservatórios de petróleo. Os modelos geoquímicos são representados por equações numéricas baseadas em propriedades físico-químicas dos minerais. Existem muitos softwares disponíveis no mercado para simular sistemas e reações geoquímicas. Os códigos são divididos em três categorias distintas: transporte acoplado de reação, especiação de modelagem e modo batch de acordo com o método numérico. Sistemas simples possuem ligações claras entre entradas e saídas de dados. Sistemas complexos apresentam múltiplos fatores que oferecem uma distribuição de probabilidade de entradas dos dados que interagem em funções específicas. As saídas produzidas como resultado são, portanto, impossíveis de prever com total precisão. Diversos grupos de pesquisa tentaram desenvolver códigos numéricos para modelagem geoquímica. Os fatores críticos para o uso desses sistemas são (i) verificação dos resultados da simulação com conjunto de dados empíricos e (ii) análise de sensibilidade desses resultados, para a construção de modelos gerais que fornecem um caráter preditivo. Este último fator é particularmente importante, pois estabelece o impacto qualitativo e quantitativo de cada parâmetro nas simulações. Assim, com os modelos numéricos simples ou complexos, são possíveis realizar várias simulações modificando um ou outro parâmetro para testar a sensibilidade na construção em diferentes cenários geológicos. Esse conjunto inclui composição e textura mineral, composição de fluidos, sequência paragenética e histórico de sepultamentos. Este trabalho traz conceitos fundamentais relacionados a este tema, bem como uma análise dos softwares comerciais disponíveis no mercado.

**Palavras-chave:** Modelagem Geoquímica, Sistema Petrolífero, Simulação Numérica

## ABSTRACT

The numerical modeling of transport and reaction was used for the understanding of the evolution of the diagenetic processes and their importance in the characterization and prediction of oil reservoir quality. Geochemical models are represented by numerical equations based on physical-chemical properties of minerals. There are many software's available in the market to simulate systems and geochemical reactions. The codes are divided into three distinct categories: coupled transport of reaction, modeling speciation and batch mode according to the numerical method. Simple systems have clear connections between inputs and outputs. Complex systems have multiple factors that provide a probability distribution of data inputs that interact in specific functions. The outputs produced as a result are therefore impossible to predict with complete accuracy. Several research groups tried to develop numerical codes for geochemical modeling. The critical factors for the use of these systems are (i) verification of the simulation results with empirical data set and (ii) sensitivity analysis of these results, for the construction of general models which provide a predictive character. This last factor is particularly important as it establishes the qualitative and quantitative impact of each parameter in the simulations. Thus, with complete numerical model diagenetic, it is possible to perform various simulations modifying one or the other parameter to test the sensitivity in the construction of these different geological scenarios. This set includes mineral composition and texture, the composition of fluids, paragenetic sequence and burial history. This work brings fundamental concepts related to this topic as well as an analysis of commercial software available.

**Keywords:** Geochemical Modeling, Petroleum System, Numerical Simulation.

## 1. INTRODUCTION

To understand of the evolution of the diagenetic processes and predict the oil reservoirs quality, numerical modeling of transport and reaction is a fundamental tool for professionals in the geoscience area (Jeppu *et al.*, 2012). Chemical properties of minerals and their interactions with fluids of different compositions is a basic of the models. In this study, geochemical models represented by numerical equations based in physic-chemical proprieties of the minerals (Baba *et al.*, 2008). Mathematical models allow simulating the behavior of water-rock interaction, providing a better understanding of the development of diagenetic reactions in time and space and its influence on the quality and variety of hydrocarbon reservoirs (Merkel *et al.*, 2005). The objective is to generate a conceptual and software tool to assist geologists and geochemists in exploration and production in their daily task of assessing exploration risks and reservoir characterization (Park *et al.*, 2015). This work has as purpose do a study of the software used in geochemical modeling.

## 2. GEOCHEMICAL MODEL APPROACH

Geochemical model is only useful as a tool for prediction if there the possibility to validate the results Qi *et al.*, 2016). A simplification of reality should treat a model and as a tool to estimate the probability that a prediction can be considered true or false (Verma, 2012). The principle of conservation of mass is applied in geochemical models. Two categories can classify the models: i) models that do not consider the transport process is referring only to geochemical reaction or simply "batch models"; ii) models that consider transport processes and geochemical reactions are called models of coupled transport and reactions (Tarcan *et al.*, 2016). Determination of geochemical reactions that predominate in a system, quantification of these results and estimate the flow rates of groundwater are examples of applications that use these models (Parkhurst & Plummer, 1993). Much software, using the geochemical reactions based on conservation of the total concentration of the components combined with the chemical equilibrium.

## 3. PROCESS SIMULATION

The coupled transport model differs from

the model geochemical reaction by adding mathematical formulas in the transport processes. The coupled transport model simulates the evolution in the geochemical system to long the time and estimates the flow path of fluid that may be 1, 2 or 3 dimensions. The equation of advection-dispersion-reaction (ADR) describes the mathematical process of reaction and coupled transport. The equation ADR predict transport within a porous medium with a constant flow rate. One of the problems associated with the concept of ADR is the dispersivity (Scheidegger, 1954) that introduce a new approach to the problem of modeling of flow and dispersion of solutes in porous media: statistical stochastic. According to Scheidegger (1954) particles of fluid not only move along the flow lines resulting from Darcy's law but are also dispersed to the sides, designated dispersivity, which appears in the equations of motion. Under some statistical assumptions, the dispersivity is constant of the porous medium. The three constants medium determines the flow of fluid through the porous medium: porosity, permeability, and dispersibility. Most programs allow calculating the precipitation/dissolution of mineral. The reactions are complexation, ion exchange, and redox reactions. The main limitation is the quality and available of thermodynamic data. Much software's have excellent databases of aqueous species and reactions in the mineral phase.

The activity coefficient of aqueous species is calculated using the Davies equation and Debye-Huckel equation. The equations of Pitzer (Pitzer, 1991) are essential for understanding the behavior of ions dissolved in natural waters such as rivers, lakes, and seawater (Stumm and Morgan, 1996; Snoeyink and Jenkins, 1980; Millero, 2006). Software that simulates kinetic reactions using different numerical methods for equilibrium systems; therefore these methods are appropriate for a set of algebraic equations and non-linear differential equations. Darcy's law (an equation that describes the flow of fluid through a porous medium) apply the Richards equation to describe the motion of estimating the water permeability (Richards, 1931).

## 4. SOFTWARE FOR GEOCHEMICAL MODELING

There are many commercially available programs to simulate systems and geochemical reactions. The primary codes are listed below. They are divided into three distinct categories: coupled transport of reaction, modeling

speciation and batch mode according to the numerical method.

#### 4.1. Coupled transport and geochemical reaction

Below is information about the programs mainly for the simulations that consider the transport processes and geochemical reactions.

##### 4.1.1. CHEMFLO

CHEMFLO to simulate the transport of water and chemical products in saturated soils, using the Richards equation (Richards, 1931) and equation convective-dispersion. The development of mathematical models makes a prediction of the behavior of contaminants and trends preferred the flow of water in the soil. Modeling in 1D, using the finite difference method implicit and explicit linearization. Richards equation and incorporates partial differential equations describing the motion of the water and transport of chemicals (Richards, 1931). The software contains an algorithm to determine the initial grid size at a certain depth. The model includes an algorithm to adjust the balance of mass and depth of wetting. The user can specify a grid size and the desired accuracy (Herrada *et al.*, 2014; Nofziger *et al.*, 1989).

##### 4.1.2. FEFLOW

FEFLOW is software for simulation of groundwater flow, mass transfer and heat in porous media. The program uses finite element methods to solve the flow equation groundwater saturated and unsaturated. Darcy's law is applied to calculate saturated groundwater flow; however, in unsaturated groundwater flow the code use Richards equation (Li *et al.*, 2017; Diersch 2005; Richards, 1931).

##### 4.1.3. Geochemist's Workbench – GWB

In geochemical reaction modeling, as the name suggests, you construct numerical simulations of reactions that might occur in the geochemical environment (Bethke, 2002). This code can model the consequences of a specific fluid reacting with a particular set of minerals. For a detailed description of such modeling, as well as a large number of fully worked examples, please see the Geochemical and Biogeochemical Reaction Modeling text, available from Cambridge University Press and book sellers such as Amazon. In The Geochemist's Workbench, you use program React to trace reaction models, and program Gplot to render

the results of reacting simulations (Bethke, 2008) graphically.

##### 4.1.4. HYDRUS-1D AND 2D

HYDRUS-1D AND 2D is a software that simulates the flow of water in 1D and 2D solute transport in saturated porous media. In the 2D version also includes an optimized algorithm parameter like Levenberg-Marquardt algorithm for estimating the inverse of the hydraulic soil. Simulate the transport of heat and solute movement involving decay reactions. HYDRUS uses the Richards equation to simulate variably saturated flow and advection-dispersion equations for heat and solute transport (Richards, 1931). The heat transport equations consider the conduction and convection current. The transport equations predict reactions without chemical equilibrium between solid and liquid phases (Li *et al.*, 2014; Turco *et al.*, 2017; Simunek *et al.*, 1999; Simunek *et al.*, 2005).

##### 4.1.5. MODFLOW

MODFLOW is the software developed by the U.S. Geological Survey first published in 1984, applied to simulate groundwater flow. The software family includes the MODFLOW: MODFLOW-SURFACT, MS-VMS, MT3D, and PATH3D. Mathematically using finite difference methods for fluid flow calculations (Ou *et al.*, 2016; McDonald, 1988).

##### 4.1.6. MODFLOW-SURFACT

The MODFLOW-SURFACT is a 3D modeling that using finite difference methods able to simulate the flow of groundwater and solute transport and flow saturated areas. It is based on USGS MODFLOW, is a code that groundwater flow most used in the world. MODFLOW, however, has certain limitations in simulating complex field problems. Additional computational modules were incorporated to enhance simulation capabilities. Recognizing the limitations of codes of contaminant transport in MODFLOW, new transport modules were developed and integrated MODFLOW-SURFACT (McDonald, 1988).

##### 4.1.7. MS-VMS

MS-VMS overcomes the difficulties encountered in MODFLOW, providing a modeling environment with rapid visualization and interpretation of data generated by MODFLOW-SURFACT. The presentation of the data can be

in two and three dimensions using a Tecplot interface (TIF).

MODFLOW-SURFACT constitutes the core of MS-VMS. MODFLOW-SURFACT through their new computational modules based on efficient algorithms for the conservation of mass overcomes the limitations and eliminates several restrictions of MODFLOW. This feature allows the user to import the MODFLOW files previously created with some little changes (McDonald, 1988).

#### **4.1.8. MT3D**

MT3D is a 3D modeling software that simulates the advective-dispersive transport and chemical reactions of dissolved constituents in groundwater. MT3D uses the modular structure of MODFLOW, with a finite difference, equation advective-dispersive-reactive for the transport of solutes and mixtures with a Lagrangian-Eulerian approach. This approach combines the power of the numerical method for eliminating numerical dispersion and efficiency calculation modification characteristics. This allows the user to build a model of flow independently. MT3D has the capability spatial discretization and boundary conditions for the transport (1) confined and unconfined aquifers, (2) layered model variables and the thickness of cells within the same layer, (3) the effects of transporting solutes from external sources like wells, rivers and recharge areas (Lautz and Siegel, 2006; Zheng, 1990).

#### **4.1.9. PATH3D**

This program can be applied in the visualization of transient flow, three-dimensional, to zones for contaminants or protection zones scenarios evaluating the effectiveness of remediation of groundwater in complex hydrogeological conditions (Zheng, 1995). PATH3D is a significant extension to the models of groundwater flow and a practical alternative to the models of contaminant transport. Its main features: (i) interfaces with MODFLOW, where the input files of MODFLOW are used directly by PATH3D, (ii) applicable to three-dimensional and transient flow in wells, rivers and aquifer recharge (Zheng, 1995). It is written in standard FORTRAN 77 for implementation on all computer platforms. PATH3D has developed Chunmiao Zheng in the University of Wisconsin-Madison, Wisconsin, with Wisconsin Geological and Natural History Survey (Anderson *et al.*, 2015; Zheng, 1995).

#### **4.1.10. RAND3D**

RAND3D is a 3D modeling software with random solute transport. This software is the same software family of MODFLOW. The models generated by RAND3D includes the following characteristics: (i) calculating the horizontal advective using different interpolation of velocity; (ii) calculating the vertical advective transport based on linear interpolation between the input vectors vertical velocity at the top and bottom each layer; (iii) dispersion calculation using dispersibility constant, longitudinal, transverse and vertical; (iv) adsorption linear calculation (delay); (v) calculating the concentrations of solute in the output grid; (vi) the ability to transient flow simulation by performing various time intervals (Zheng, 1995). Vector files of velocity and flow are created using a preprocessor called PREMOD3D. PREMOD3D the software uses the input files of MODFLOW creating velocity vector files, which are used to perform RAND3D (Mulligan and Yong, 2004; Zheng, 1995).

#### **4.1.11. PHREEQC**

PHREEQC provides an efficient method for numerically simulating the movement of solutions through a column or 1D flow path, with or without the dispersion effects. PHREEQC models generate initial composition of the aqueous, gaseous phases and solid phases, reversible and irreversible chemical reactions (Pitzer, 1991). The software allows inverse modeling to compensate for the chemical changes that occur when water develops along a flow path. PHREEQC allows uncertainty limits at being defined for all analytical data, so that the model inverse satisfies the molar balance of each element on its valence state and the charge balance of each solution, while the adjustment of analytical data required to be within a range of uncertainty (Pitzer, 1991). The input data in PHREEQC is completely free based on chemical symbols. PHREEQC is an application program geochemistry and hydrogeochemical (Charlton and Parkhurst, 2011; Parkhurst, 1999).

#### **4.1.12. TOUGH2**

TOUGH2 is a program used for the numerical simulation of fluids and dimensional heat flow multiphase mixtures of several components in porous and fractured. Its main applicability involves geothermal reservoirs, isolation study of nuclear waste, environmental assessment and remediation, flow and transport in saturated media and aquifers. The TOUGH2

was released in 1991 (Pruess, 1991), providing five different fluid properties in modules called "EOS" (equation of state - EOS1" - "EOS5). The new version 2.0 includes new fluid properties (EOS7; EOS7R; EOS8; EOS9; EWASG). TOUGH2 solves equations of mass balance and energy in fluids and heat flow in multiphase systems and multiple components (Pitzer, 1991).

The advective fluid is described by Darcy's law and, moreover, there is the diffusive mass transport in all phases (Rinaldi and Nespoli, 2017). The description of thermodynamic conditions is based on the assumption that equilibrium location of all phases. The finite difference is a mathematical expression applied in numeric methods (Arnaldsson *et al.*, 2014; Bonduá *et al.*, 2012; Narasimhan *et al.*, 1976).

#### 4.1.13. TOUGHREACT

The first version of TOUGHREACT was developed by Xu and Pruess 1998, introducing reactive geochemistry heat flow and multi-phase fluid in TOUGH2 (Pruess, 1991). TOUGHREACT been enhanced with addition: (i) interaction mineral-water-gas and reactive transport under boiling conditions; (ii) improvements in the model for the activity of aqueous species; (iii) diffusion coefficients of gaseous species calculated function of pressure, temperature and molecular properties; (iv) reactive surface area of the mineral -related or fractured porous media; (v) porosity, permeability due to precipitation/dissolution. The flow parameters are based on the codes TOUGH2 V2, with some extensions (Pruess *et al.*, 1999). The TOUGHREACT is applied in one-, two-, or three-dimensional geologic domains in heterogeneous physical and chemical. The temperature and pressure are monitored by the thermodynamic equation of state (EOS) (Pitzer, 1991).

The equations that govern multi-phase fluid flow and heat are deriving from the principle of conservation of mass (or energy) (Pruess 1987; Pruess *et al.*, 1999). For transport, the equations are written in terms of the concentration of total dissolved chemicals. The advective and diffusive process is considered for gaseous and aqueous species. These equations are solved by the Newton - Raphson interaction as implemented in the code TOUGH2 (Wolf *et al.*, 2016; André *et al.*, 2015; Pruess 1991).

## 4.2. Geochemical speciation modeling

The concept of speciation is applied in

many chemical systems in special to aqueous solutions (Graeme *et al.*, 2009). Such solutions include natural water systems such as sea, river, ground and lake waters. The chemical speciation of a system is determined experimentally by analytical methods. The geochemical speciation modeling predicts this species and separates according to a charge of the ions, forming intermediate species undetectable by analytical instrumentation. The advantage of geochemical speciation is the determination of the concentration of very dilute intermediate species (Bernhard, 1999).

### 4.2.1. Geochemist's Workbench – GWB

GWB use modules SpecE8 and GSS in "React Mode" for speciation model. The user sets the initial condition (concentration of species) of the geochemical system in thermodynamic equilibrium. So, the GWB start the calculation and necessary interactions that lead to speciation model. When GWB finished the simulation, output data is generated.

The information contained in this file are temperature, pressure, pH, ionic strength, water activity, the mass of solvent, dissolved solids, solution density and mass of the rock. An aqueous species list with all solutes presents in the simulation is formed. The "State Mineral Saturation" of the fluid with the mineral is formed in the system. Three relationships occur: i) mineral and solution are in equilibrium -  $IS = 1$ ; ii) super-saturation -  $IS > 1$  and iii) under-saturation -  $IS < 1$  (Bethke, 2008). The GWB solve the equations using the Newton-Raphson method (Shevalier *et al.*, 2014; Kong *et al.*, 2013).

### 4.2.2. MINTEQA2

It is a model of speciation in geochemical equilibrium able to calculate quantities dissolved, adsorbed on the solid or gaseous phase in rebuilding a geological environment. MINTEQA2 includes a broad base of reliable thermodynamic data, which is also accessible PRODEFA2 (is the interface MINTEQA2), an interactive program designed to be executed before the MINTEQA2 with the purpose of creating input files needed for the MINTEQA2.

Uses equations of Debye-Huckel and Davies equations to calculate the activity coefficients (Reddy *et al.*, 2014; Serkiz *et al.*, 1996; Allison *et al.*, 1991).

### 4.2.3. PHREEQC

PHREEQC is a software written in

programming languages C and C++ designed to perform a wide range of geochemical calculations. PHREEQC implements various types of models in the aqueous phase: ion association models, models of interaction between the ions using the Pitzer equations and a model of specific ionic interaction (Pitzer, 1991).

The PHREEQC is capable of (i) calculate the saturation index and speciation (ii) calculates the reactions in "batch model" and transport one-dimensional (1D), mixing solutions, and changes in temperature and pressure. Use the Pitzer model for high salinity water that is outside the range of application of the Debye-Huckel theory (Pitzer, 1991). The use of the Peng-Robinson equation is implemented to calculate the solubility of gases at high pressure. Specific volumes of aqueous species are calculated by the dielectric properties of water and the ionic strength of the solution (Pitzer, 1991). The software use method of numerical integration allowing the solution of ordinary differential equations, which can be generalized for the reconstruction of three-dimensional trajectories (Pitzer, 1991). In an additional package, the PHREEQCI has a graphical interface for Windows and can to perform all tasks PHREEQC (Charlton and Parkhurst, 2011; Parkhurst, 1999).

#### 4.2.4. GEODELING

The own code speciation has application in physical, chemical aqueous and geochemists useful tool with intuitive and interactive interface. GEODELING is planned as: i) speciation model – solving reaction as equilibrium reactions with the help of matrix reduction method; ii) extending options on activity correction method – Debye-Hueckel, B-dot, Pitzer and Davies and iii) adding kinetic reaction to the speciation model – recompose the speciation model to solve mineral-water interaction (Klunk *et al.*, 2019; Kehew, 2001).

#### 4.3. Geochemical Reaction (Batch Systems)

Below is information about the programs mainly for simulations of processes of geochemical reactions in a batch system:

##### 4.3.1. Geochemist's Workbench – GWB

The GWB was developed by the department of geology at the University of Illinois at Urbana-Champaign in 1978. It is currently marketed by "Aqueous Solutions LLC". GWB

makes quick work of the most commonly encountered in geochemical modeling: (i) calculate the saturation index estimating the distribution of aqueous species; (ii) make the balance of the reactions and the amount of the aqueous species, minerals, and gases; (iii) calculates the stability and solubility diagrams (Bethke, 2002). Mathematically, the GWB uses finite difference methods to calculate the reactions.

The activity coefficient is calculated by the equation "B-dot" which is an extension of the Debye Hückel equation and supplemented by model Harvie-Møller-Weare to highly saline solutions such as brine (Pitzer, 1991). The saturation index of minerals is calculated using models of Debye and Hückel Harvie-Møller-Weare (Bethke 2002; Pitzer, 1991). The GWB apply the concept of the chemical equilibrium of two different ways. The first concept, derived from the classical theory of thermodynamics, affirm that equilibrium state is the lowest free energy for a system. The second concepts, due to the field of chemistry in aqueous solution, affirm that the equilibrium state of reversible and irreversible chemical reactions of a system are equal (Pitzer, 1991).

The steady state of a system is described as the sum of all geochemical reactions that are taking place within each species dissolved. To solve the equilibrium of an initial system, the GWB determines which reactions are more likely to happen, and to what extent they occur (Bethke, 2008).

##### 4.3.2. SOLMINEQ.88

Geochemical modeling based on equilibrium and thermodynamically irreversible processes, to understanding water-rock interactions, and predict its consequences. This program is useful for modeling geochemical interactions in sedimentary basins and oil reservoirs. SOLMINEQ.88 is written in Fortran-77. Uses the Pitzer equations to perform the calculations of activity coefficients, calculate the pH and solubility of minerals in temperatures from 0° at 350°C and pressure 1-1000 bar (Pitzer, 1991). SOLMINEQ.88 predict the effects of ion exchange, adsorption/desorption and dissolution/precipitation of solid phases.

The restrictions may be related to the chemical and mineral incomplete, as well as uncertainties in equilibrium constants of aromatic species and minerals (Evans *et al.*, 2013; Talman and Perkins, 2009; Kharaka *et al.*, 1988).

### 4.3.3. EQ3/6

EQ3/6 is a software package for geochemical modeling of aqueous systems. This report describes version 7.0 (Kong *et al.*, 2013). The significant components of the package include: i) a speciation-solubility code; ii) EQ6, a reaction path code which models water/rock interaction or fluid mixing in either a pure reaction progress mode or a time mode; iii) EQPT, a data file preprocessor; iv) EQLIB, a supporting software library and five supporting thermodynamic data files (Kumar *et al.*, 2017).

The software deals with the concepts of thermodynamic equilibrium, thermodynamic disequilibrium, and reaction kinetics. The five supporting data files contain both standard state and activity coefficient-related data. Three support the use of the Davies or B-dot equations for the activity coefficients; the other two support the use of Pitzer's equations (Wolery, 1992; Wolery and Daveler, 1992). The temperature range of the thermodynamic data on the data files varies from 25°C only to 0-300°C.

EQPT takes a formatted data file (a data file) and writes an unformatted near-equivalent called a data1 file, which is actually the form read by EQ3NR and EQ6. EQ3NR is useful for analyzing groundwater chemistry data, calculating solubility limits, and determining whether specific reactions are in states of partial equilibrium or disequilibrium. It is also required to initialize an EQ6 calculation. EQ6 models the consequences of reacting an aqueous solution with a set of reactants which react irreversibly. It can also model fluid mixing and the consequences of changes in temperature.

This code operates both in a pure reaction progress frame and in a time frame. In time frame calculation, the user specifies rate laws for the progress of the irreversible reactions. Otherwise, only relative rates are specified (Aradóttir *et al.*, 2012). EQ3NR and EQ6 use a hybrid Newton-Raphson technique to make thermodynamic calculations. This is supported by a set of algorithms which create and optimize starting values.

EQ6 uses an ODE integration algorithm to solve rate equations in time mode. The codes in the EQ3/6 package are written in FORTRAN 77 and have been developed to run under the UNIX operating system on computers ranging from workstations to supercomputers. This report describes in general terms how to install the software, with specific instructions on how to install it on systems running UNIX (Snæbjörnsdóttir *et al.*, 2018).

## 5. WATER-ROCK INTERACTION: MODELING OF COMPLEX AND SIMPLE SYSTEMS

Simple systems have clear links between inputs and outputs. If certain knowable conditions are met, there is a distinct function that maps the inputs to the outputs (Reed, 1982).

Complex systems are different. They feature multiple actors that offer up a probability distribution of inputs that interact in context-specific functions with partially knowable forms and indeterminate weights. The outputs that are produced as a result are therefore impossible to predict with full accuracy (Cotta and Schaefer, 2017). As a result of the different nature of simple and complex systems, the approach necessary to succeed when working with each is different. In particular, working with simple systems requires knowledge of the facts (Farnell *et al.*, 2018).

Equilibria between solutions of aquifers/reservoirs and their host rock minerals should be incorporated into geochemical models of complex natural systems (Appelo and Postma, 1996). In general, in shallow porous media (i.e., aquifers), fluids are less likely to be in equilibrium with mineral phases because temperatures are lower, reaction rates are relatively slow and fluid residence times are generally short transport rates (Busenberg and Plummer, 1982). In deeper systems, such as oil reservoirs, water more often balances with host rock minerals because temperatures are higher, reaction rates are faster, and residence times are longer (Drever, 1997). Many surfaces and low-temperature groundwater solutions are in equilibrium with the phases of calcite or amorphous silica, such as chalcedony. Instead of assuming that a system is in equilibrium, a modeler must evaluate the balance of mineral fluid separately for each relevant phase in the system (Greaser, 2004).

The three approaches to applying the redox equilibria and fluid-mineral (Bethke, 2008):

1. Suppose the dissolution/mineral precipitation reaction has enough time to reach equilibrium.
2. Suppose the dissolution/mineral precipitation reaction does not reach equilibrium and does not occur appreciably during the simulation duration of the model.
3. Assume that the dissolution/mineral precipitation reaction does not reach equilibrium, but occurs substantially during the duration of the model simulation.

In assessing the equilibrium state of the individual dissolution/mineral precipitation

reactions in the system, the modeler should consider the collective effects of the time scale of interest, fluid transport rates, average properties, temperature, mineral kinetics, and other factors (Metz *et al.*, 2003). The addition of complexity to the fluid/rock equilibrium assumptions required to construct these models are severe deficiencies in the analytical data used for model input (Morse and Arvidson, 2002; Zhu and Anderson, 2002): i) reservoir host rock compositions are often absent or incomplete; ii) fluid chemistries may undergo significant chemical changes during transport upwards; iii) fluid chemistries and mineral compositions are often sampled in completely different places; iv) dissolved SiO<sub>2</sub> content, a crucial component in restricting fluid equilibrium with aluminosilicate reservoirs, is often omitted from fluid analyzes. Dissolved SiO<sub>2</sub> also serves as an excellent geothermometer and may be useful in determining whether the sample has been contaminated by drilling fluids, mixed with other fluids or has been diluted by the condensate of water vapor in the pipeline during production.

## 6. CONCLUSIONS

The present study of the simulation codes coupled to the geochemical models were divided into three distinct categories: speciation modeling, batch mode and coupled transport of reaction. The simulations in have two objectives: i) varying the geological time interaction to check the chemical stability of minerals and ii) varying the temperature of the reaction medium to verify the saturation index of the mineral. This non-steady state of initial water is a result of the difference between the number of solutes and the number of minerals present in the geological environment. Thus, there is a sharing of these minerals with the chemical element causing dissolution, being evident the negative saturation index. Once the simulations advance and the waters are flowing from the salt dome toward the sandstone, reaction fronts begin to form where the two waters are being mixed. Water entering the sandstone by the salt dome creates a pattern of different diagenetic alteration of reactions that existed between the steady state water and sandstones. Users must be cautious when choosing geochemical modeling software, as an essential factor in determining a simulator is to know the temperature range that will be used. With the temperature information, the user should do a preliminary study with the available codes for verifying the convergence of results to the observed diagenetic reactions.

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