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# Experimental Validation of a Numerical Model - Application of an Open Source Algorithm towards Geothermal Conditions

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## ABSTRACT

Numerical modeling of at least real conditions needs to be confronted to experiments. Regarding some questioning of the geothermal energy use, in this study, a numerical model is built up. This structure and the development of the modular model are presented. It can calculate the chemical water-rock interaction within the flow and is set up in an open source environment using PhreeqC for the chemistry and Elmer for the transport (3D). The coupling of these ones, being sequential, allows to modeling the time evolution of hydraulic and transport properties induced by the chemical environment evolution. So far, for the validation of the numerical model a 1D and 2D case are considered.

## 1. INTRODUCTION

For centuries the geothermal source were used for a kind of healing or for balneological purposes. In 1904 in Larderello (Tuscany) the first power plant for producing energy out of the thermal water becomes operational. Therefore the geothermal fluid has to be produced and the heat will be deprived. The fluid itself is in the reservoir formation in equilibrium with the enclosing rock formation. When this fluid will be mined it undergoes a pressure release and a heat extraction. Therefore the thermodynamic properties and the chemical composition are changed. Re-injecting of this modified fluid into the target formation can lead to significant changes in permeability. At worst the reservoir formation may be affected by dissolution and/or precipitation of minerals, small particle release and capture (Chang and Civan, 1997).

Due to that it is necessary to differentiate between (1) mechanical and (2) chemical processes. A redistribution of small particles (e.g. quartz, feldspar) belongs to the category (1). Hereby through the flow of the fluid fine particles disentangles and settle down elsewhere. This particle movement may cause an opening or closing of porous space (Ochi and Vernoux, 1998; Kühn et al., 1998). Due to the (2) chemical processes the modified water hits the reservoir rock and consequently chemical interactions occur (Ochi and Vernoux, 1998). In the close vicinity of the borehole (Fig. 1) mineralogical modifications are expected, because there is the spot of the media fluid and minerals. Regarding further distances the reaction front should thin down.

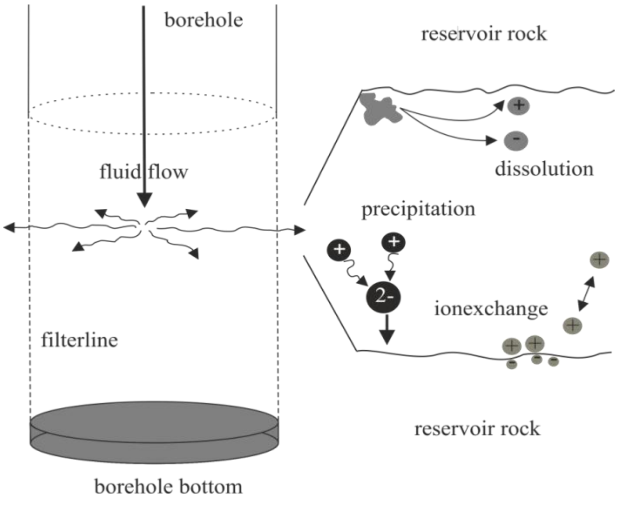

Figure 1: Scheme of the processes in the nearfield of the injection well.

The relevant (2) geochemical processes for this research are the dissolution and the precipitation of minerals. But also ion exchange, sorption and complexation are phenomena which should be mentioned (Yeh and Tripathi, 1989). These interactions, however, are very site-specific and require the use of numerical modeling and adapted laboratory experiments in order to understand the occurring processes in detail. This work shows how to establish a geochemical transport model and further to validate it with suitable experimental tests.

## 2. METHODOLOGY

For a development of the multidimensional numerical model the idea is to couple open source codes by using an operator splitting. The result is a modular approach (Fig. 2) with already available codes, which compounds result in a new application (Dimier, 2011). This splitting can be combined with a sequential iterative approach (SIA) between hydrological and chemical equilibrium computations (Yeh and Tripathi, 1989).

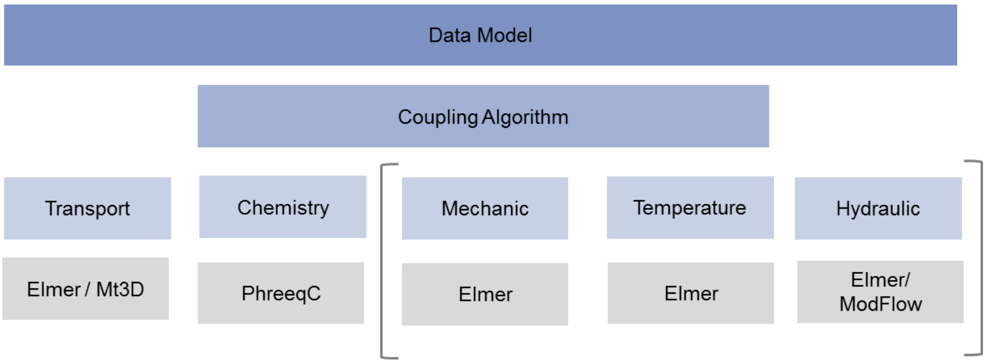

**Figure 2: Modular structure of the model.**

## 2.1 Elementary Tools

The programs are normally utilized for specific applications like the chemistry, the transport or the temperature distribution. Through the coupling it is possible to get a kind of multi-physics application (Montarnal et al., 2005).

The common chemical modelling programs are based on equilibrium formulation, there exist e.g. WATEQ4F (Ball and Nordstrom, 1991), MINTEQA2 (Allison et al., 1991), EQ 3/6 (Wolery, 1979), Chess (MINES, Paris), TOUGHREACT (Xu et al., 2006), CrunchFlow (Steefel, 2009) and PhreeqC (U.S. Geological Survey). At this, PhreeqC is chosen and the reasons are: It is an open source code, the reaction equations are written in the syntax of chemical formulas and it has a GUI (Merkel and Planer-Friedrich, 2009). Additionally, it is the most widely used geochemical model, it gives a wide variety of geochemical aqueous calculations, it is based on an equilibrium chemistry of the aqueous solutions interacting with e.g. mineral phases and includes the modelling of kinetically controlled reactions. The program has a couple of databases which are case-specific selectable for low and high ionic strength (Parkhurst and Appelo, 1999). The addenda of them are very helpful. For geothermal related experiments with a high-saline fluid (high ionic strength) the database pitzer.dat can be selected. But hereby limitations are gaps in the database of some considered minerals of reservoir rocks, like e.g. the kinetic of hematite.

For the Pre-processing, associated to the finite element code, the mesh generation is implemented by the open source code named Gmsh developed by Geuzaine and Remacle (2009). Therefore a Python-module has to be defined to manipulate e.g. the mesh elements and bodies, which are retrieved from the mesh file. Via this Python interface the mesh bodies become objects which can be associated to material properties or aqueous states characterizing the problem to be modelled.

The flow, the transport and the temperature can be described by Elmer. This code is written by the IT Center of Science and it uses a finite element formulation. The code involves the diffusion, convection and reactions which are needed for the research topic. Elmer being interfaced with major commercial mesh generators, depending on user’s needs, meshes from different sources can be used (Raback et al., 2014).

The Post-processing, thus the visualization application is made with Paraview. It is also open-source, originally created by Kitware together with Jim Ahrens of the Los Alamos National Laboratory (Henderson et al., 2004).

The used programming language for the data model and for the coupling of all the previously mentioned codes is Python. Widely used in the scientific and numeric community, it is an interpreted interactive, object-oriented language. Python has e.g. dynamic typing, binding, modules, classes and an automatic memory management. Beside the use of it as a tool manager, the supply of a functional graphical user interface but even though the scientific computing is relevant. Additional strength of Python is to create user defined functionalities (Beazley, 2008).

## 2.2 Coupling Algorithm

For example, to match with PhreeqC requirements, a generic species class has to be created (Yeh and Tripathi, 1989). After that a master species and a secondary species class will inherit from that ancestor to enable part of the chemical problem definition. Thereby a feature of Python allows the definition of a case study through class instantiation and module parameterization. This script contains all data being read through the interpreter. In that way two specific data files, called shared objects, of Elmer and PhreeqC were generated: WElmer.so and WPhreeqc.so (Dimier, 2011).

Over a wrapping process Elmer and PhreeqC functionalities become part of Python modules. The type of wrapping for which Python is suitable, is based on a memory exchange. Thereby codes are integrated in the platform as dynamic libraries and this optimized CPU costs (Montarnal et al., 2005). For a possible communication between the software and Python, the first step is to create C wrapping functions. These functions allow data manipulation between the tool itself and the Python interpreter and based on the specific structures of each program. Thereby the initialization is the first method, where specific data files are created by Python. This allows launching the software, reading the file and generating suitable structures. E.g. the time step is chemistry driven and will be managed by Python. Similar to that, we created a Python module to manipulate the mesh, which satisfies the gmsh-format.

## 3. GEOCHEMICAL APPROACH

The used Software PhreeqC assumes that the dissolved species are in thermodynamic equilibrium. But minerals often do not react to equilibrium during the predefined time frame. When a reaction is kinetically controlled it generates concentration changes according to the rate equation:

$$\frac{dm_i}{dt} = c_{i,k} R_k \tag{1}$$

Where $c_{i,k}$ is the stoichiometric coefficient of species $i$ in the kinetic reaction, and $R_k$ is the overall reaction rate for substance $k$ [mol/kgw/s] (Parkhurst and Appelo, 1999). This rate has to be numerically integrated over a time period; therefore PhreeqC enables the use of a Runge-Kutta or the CVODE Algorithm (Cohen and Hindmarsh, 1994).

The rate for a kinetic reaction of solid or minerals is:

$$R_k = r_k \frac{A_0}{V} \left( \frac{m_k}{m_{0,k}} \right)^n \tag{2}$$

$A_0$ is the initial surface area of the solid, $r_k$ is the specific rate, $V$ is the amount of solution, $m_{0,k}$ is the initial moles of solid, $m_k$ is the moles of solid at a given time, $(m_k/m_{0,k})^n$ is a factor to account for changes in $A_0/V$ during e.g. dissolution. PhreeqC uses the keyword RATES for loading of the needed rate expressions $r_k$ (Parkhurst and Appelo, 1999). Hereby the databases have a different completeness regarding the necessary minerals. For calcite, quartz and feldspar exists some kinetic algorithm which is usable for the numerical modeling. The dissolution and precipitation of calcite ($CaCO_3$), which is for this research of interest, is given by the equation of Plummer et al. (1978):

$$r = k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3 a_{H_2O} - k_4 a_{Ca^{2+}} a_{HCO_3^-} \tag{3}$$

Where $a$ represents the activity, $k_1$, $k_2$, $k_3$ are the forward rate constants and $k_4$ the backward rate, as a function on temperature. Therefore, for the forward rates of calcite three main reactions are occurring. These steps are depending of the pH-value (Plummer et al., 1978):

$$\begin{aligned} &CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \\ &CaCO_3 + H_2CO_3^* \leftrightarrow Ca^{2+} + 2HCO_3^- \\ &CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^- \end{aligned} \tag{4}$$

As mentioned before the activity is a relevant variable for the kinetic of calcite. The activity defines the influence of the salt content to the equilibrium constant.

$$a_i = f_i * c_i \tag{5}$$

Where $f_i$ is an ion-specific correction factor and $c_i$ the concentration of the Ion $i$.

Activity coefficients of aqueous species are defined by approximation equations like the Davies-Equation or here the extended Debye-Hückel equation:

$$\log f_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} \tag{6}$$

Where $z_i$ is the ionic valency of aqueous species $i$, $A$ and $B$ are parameter dependent on temperature and $a_i$ is an ion-specific parameter (Merkel and Planer-Friedrich, 2008; Parkhurst and Appelo, 1999).

The validation of (6) for calculating the activity coefficient depends on the ionic strength $I$ of the fluid (Debye und Hückel, 1923):

$$I = \frac{1}{2} \sum_i c_i (z_i)^2 \tag{7}$$

For these solutions some assumptions have to be made. Hereby the ionic interactions caused by the Coulomb forces, the ionic size do not change with the ionic strength and ions with the same sign have no interaction. These assumptions are valid for ionic strength smaller than 0.5 mol/kg, therefore the Debye-Hückel equation is valid ($I < 0.005$ mol/kg). With increasing ionic strength the solver can be the extended Debye-Hückel, the Güntelberg and the Davies-Equation. Above 0.5 mol/kg, which are values of a geothermal fluid e.g. in the Upper Rhine Valley, the assumptions are invalid. Additional an increasing part of hydrate covers were build and resulting the amount of free water-molecules are getting smaller and the concentration of the activity coefficient rises. With this character of the fluid the Pitzer-equation is valid (Merkel and Planer-Friedrich, 2008).

## 4. HYDROLOGIC TRANSPORT EQUATION

The main mechanisms for the transport are advection, diffusion and dispersion. Beside that the chemical substance be defeated by processes like the adsorption/desorption, decay and the dissolution/precipitation. Thereby the sorption and the decay are not mentioned, because these processes are not relevant for this research. The transport equation which should be solved:

$$\frac{d_c}{d_t} = -\nabla(uc) + \nabla(D\nabla c) + S \tag{8}$$

Where $u$ is the pore space velocity, $c$ the concentration, $D$ the diffusion/dispersion coefficient, $t$ the time, $\nabla$ the nabla-operator in three dimensions $((d/d_x)/(/d/d_y)/(d/d_z))$ and $S$ the source/sink term (Rausch et al., 2005).

The diffusive motion is caused by the Brown'sche molecular movement and can be described by the Ficks Law. The first Ficks law is valid for steady state processes and whereby the second Ficks law considers the concentration over time. In the porous media the ions have to flow through the channels of the rock. The effective diffusion coefficient contemplates these effects with the impedance factor/tortuosity:

$$D^* = D_m \frac{\theta}{\tau^2} \tag{9}$$

Where $D^*$ is the effective diffusion coefficient, $D_m$ the molecular diffusion, $\theta$ the porosity and $\tau$ the tortuosity (Lege et al., 1996).

The advective transport of a substance is working by the flow of the groundwater, even though the dispersion acts as distributer and concentration reducer. This process can affects in the longitudinal (flow direction) and the transversal direction (orthogonal to the flow direction). The simulation with the software Elmer is based on the governing equation after Zheng and Wang (1999) with the assumption, that the transported quantity is carried by an incompressible fluid:

$$\frac{\partial(\theta C^k)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial(C^k)}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(\theta v_i C^k\right) + q_s C_s^k + \Sigma R_n \tag{10}$$

Where $C_k$ is the dissolved concentration of species $k$, $\theta$ is the porosity of the medium, $t$ is time, $x_{i,j}$ is the distance along the coordinate axis, $D_{ij}$ is the hydrodynamic dispersion coefficient tensor; $v_i$ is the pore water velocity; $q_s$ is the volumetric flow rate representing sources (+) or sinks (-), $C_s^k$ is the concentration of the source/sink flux for species $k$ and $\Sigma R_n$ is the chemical reaction term. Assumption thereby is the Darcy regime of the fluid velocity.

## 5. EXPERIMENTAL SETUP

A flow through experiment is needed for the validation of the model, therefore a reliably experimental design. The requirements are (1) reproducible results and (2) relatively fast implementation of the experiments. Therewith the modeling results can be fixed to the experimental ones.

The setup itself consists out of a synthetically sample with known parameters like the porosity (6%) and the hydraulically conductivity (have to be determined in pre-trials). This body is split into two parts; one upper and one lower one, and between them one layer is built with a defined mineral phase (Fig. 3). The material of the synthetically sample is a Borosilicate developed by the company ROBU (Tab. 1).

**Table 1: Chemical composition of the Borosilicate (ROBU, 2014).**

| Element | $SiO_2$ | $B_2O_3$ | $Na_2O_3$ | $Al_2O_3$ | CaO | Cl | MgO | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| Weight percentage[%] | 80,60 | 12,60 | 4,20 | 2,20 | 0,10 | 0,10 | 0,05 | 0,04 |

The layer, which is built-in between the two Borosilicate parts, is out of a Calcite-powder and some glass balls amongst them. The thickness of this layer depends on the possibility of the fitment with the practical experience. Pressure and temperature conditions are: Room conditions in the laboratory (20°C and the hydraulic pressure of the hydrostatical height by the head of water). The chemistry of the water consists out of a hydrochloride acid solution. Thereby the background is a fast solution of the calcite layer.

$$CaCO_3 + 2HCL \rightarrow CaCl_2 + H_2O + CO_2 \tag{11}$$

After the flow through of the solution and the dissolution of the layer the $Ca^{2+}$ and the Cl will be detected at the outlet of the cell. Thereby the Cl is utilized as a Tracer. The chemical components will be measured by ICP-OES ($Ca^{2+}$) and photometer (Cl). Within these measured chemical concentrations the modelled breakthrough curve can be checked and if it is necessary the model hast to be adjusted.

### 5.1 Orientation of the Layer

The layer can be built-in in different orientations. At first the horizontal option without any measure equipment installed, see point 5.2) is selected. There exists no angle of the calcite layer and the geometry is as simple as possible. This mirrors in the modelling, hereby it is modelled as a 1D case. The 2D modification is also a horizontal layer but the seismic tubes are installed, so the geometry gets more complicated. If the layer will be built-in with an angle (the value has to be determined within the feasibility) and tubes are installed, a 3D case can be considered.

### 5.2 Seismic Measurements

The dissolution of the calcite layer can be detected by seismic measurements repeated in time. Changes in amplitude and travel time are expected due to variations in porosity and in mechanical defect occurring at the interfaces where dissolution occurs. A reference measurement will be performed without any disruption of the body as a whole. The instruments from the KIT-AGW can be located at the surface of the cylindrical body. Further measurements will be carried out during dissolution processes; special care will be taken in order to avoid disrupting the flow. Data will be collected after the experiment as well.

Some seismic equipment is currently prospected in order to position waterproof and acid-resistant sensors closer to the calcite body, in small boreholes. These holes will be designed to limit disturbances of the fluid flow. For the modelling of that two possibilities are considered: (1) the tubes have a Kf-value of “impermeable”or (2) they can be modeled with varied boundary conditions and with another grid. These options have to be estimated by the experimental results.

## 6. PRELIMINARY RESULTS

### 6.1 Mesh Generation

A first step was to build up a mesh for the cylindrical body. Therefore the program code is generated with the software Gmsh. The mesh itself was generated as a structural one, for the best fitting to the present problem (Fig. 3a). Figure 3b shows the cylindrical body with the calcite layer in the horizontal version. An inclined layer will be additional created for getting a more complicated symmetry inside the model, here displayed in an exorbitant presentation (Fig. 3c).

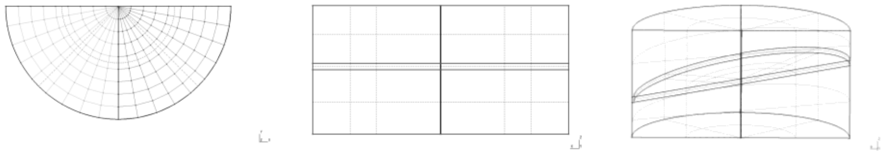

**Figure 3: 3a (left), view within the z-axis of the mesh, 1b+c view within the x,y plane. 1b (middle) with the horizontal layer, 1c (right) with the inclined layer.**

For the first runs the chemistry is chosen like mentioned before. The kinetic of the calcite dissolution is given in the database e.g Phreeqc.dat, Wateq4.dat after Plummer et al., (1978). Some parameters should be validated with the first experimental results, which are kinetically/non kinetically dissolution of calcite and open/closed system.

### 6.2 Simulation

There is build up a simulation to see how the experimental setup will behave. Concerning the simulation duration, key parameters are the pH-value of the inlet solution, the permeability and the porosity of the various materials. Hereafter, for a calcite layer, perpendicular to the flow and with the tube location taken into account, we plot the calcite amount after four days of simulation (Fig. 4). The pH has been fixed to 3 and the velocity is of 1.e-6 m/s.

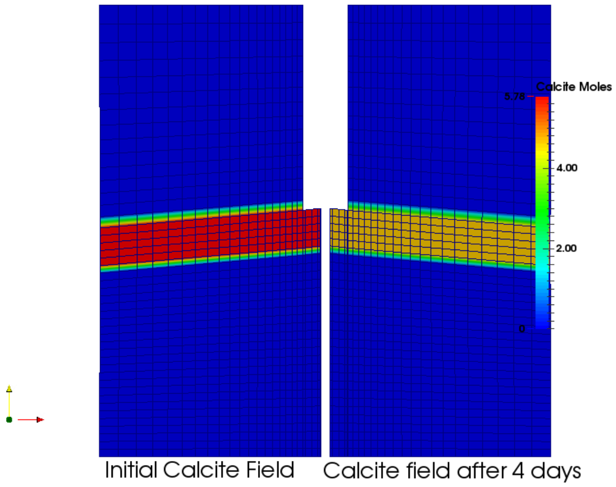

**Figure 4: Simulation of the calcite dissolution. Left: Initial concentration, right: after 4 days.**

Considering those numerical results, which doesn't take the fault porosity evolution, and making an extrapolation of them, we would reach the complete calcite dissolution after two weeks duration of the experiment. Once the different materials will be characterized, we will use the simulation to make a coarse estimation of the necessary experiment duration.

## 7. DISCUSSION AND OUTLOOK

The presented research serves as a framework for the modeling. It comes originally of the $CO_2$ Storage modeling, but is transferrable to geothermal question formulations regarding the near surface geothermal energy; the borehole heat exchangers and the deep geothermal energy use. A closer look to the deep geothermal energy, mentioned before, the model is a base for an injection or production well and therefore the environment of the reservoir rock in the near field of the wells.

Here the built-up of the model is shown and the first values of the geochemical flow in these different arranged bodies are computed. For a better adaption to the real conditions the performance of the experiments are necessary. Hereby the planned seismic measurements are possible methods to measure the dissolution of the mineral phase. The background therefore is a feasible up-scaling to geothermal reservoirs in which a chemical stimulation was done and the results have to be checked: if the chemistry has changed in the target formation especially if the porosity has been enhanced.

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