NON-ISOTHERMAL MULTIPHASE FLOW AND MULTICOMPONENT REACTIVE TRANSPORT MODELS IN POROUS MEDIA

R. Juncosa, V. Navarro, J. Samper and J. Delgado

* Departamento de Tecnología de la Construcción. E.T.S. de Ingenieros de Caminos.
Universidad de La Coruña
Campus de Elviña s/n. 15192 La Coruña, Spain
e-mail: juncosa@iccp.udc.es, web page: http://hydra.udc.es

Key words: Model, Multicomponent, Multiphase, Flow, Reactive, Transport. Repository.

Abstract. : The FEBEX project (Full Scale Engineered Barriers Experiment), was promoted by ENRESA and financed by the European Commission to study the behavior of the near field of a high-level radioactive waste repository (HLW) in crystalline rock. The FEBEX experiment has the multiple objective of demonstrating the feasibility of constructing and assembling the engineered barriers and of developing methodologies and models to evaluate the thermo-hydro-mechanical (THM) and thermo-hydro-geochemical (THG) behavior of the near field. To fulfill the needs of the FEBEX project, a THG numerical code was developed, FADES-CORE. FADES-CORE [14] allows thermo-hydro-geochemical simulation of unsaturated porous media with multiphase flow. The code has the following characteristics: The soil is comprised of a solid core (mineral phases), a liquid phase (mobile water, dissolved air and solutes) and a gas phase (vapor and dry air). The code solves the equations of water and air flow and solute transport, heat transport and chemical reactions. Chemical reactions include: aqueous complexation, acid-base, redox, cation exchange, adsorption, dissolution-precipitation and gas dissolution/exolution. Radioactive decay reactions and anion exclusion are also considered. Here we present the physical and mathematical formulation of the problem as well as the main numerical characteristics of FADES-CORE. The code has been developed by adding solute transport and geochemical subroutines to the existing code FADES [10]. FADES is a code that solves the thermo-hydro-mechanical (THM) behavior of porous media. Therefore, FADES-CORE also allows for the simulation of the mechanical process. After a thorough verification, the predictive ability of FADES-CORE has been checked against laboratory tests designed to study and understand the processes that take place in the clay barrier under controlled conditions. In these tests it is necessary to quantify evaporation-condensation processes taking place near the heaters. The thermal-hydraulic cells, a “mock-up” test and an “in situ” test (under natural conditions) have been modeled and provided excellent results [13] and [15].
1 INTRODUCTION

The study and modeling of the multiphase flow and transport in porous media has a long history in petrochemical engineering and geothermy. There are multiphase flow codes developed within the framework of the mechanics of unsaturated soils which solve the non-isothermal multiphase flow linked to deformations in the solid skeleton. As an example we may cite: CODE-BRIGHT [5], COMPASS [8] and FADES [10]. These tools have recently started to be used in underground hydrology. The family of codes derived from the TOUGH2 code [4] stand out from among the existing codes as they solve the non-isothermal multiphase flow by applying the method of integrated finite differences. Very few codes are able to solve the transport of reactive solutes in addition to the non-isothermal multiphase flow. One of these is TOUGH2-CHEM [6] which has been derived from TOUGH2. Xu and Pruess [12] have recently developed TOUGHREACT based on TOUGH, although it is still in the testing and validation stage. Lichtner [7] developed the MULTIFLO code and the most recent design was by Juncosa [14] who has developed the FADES-CORE code by adding the thermal-hydro-mechanical code FADES [10] and the flow and reactive transport code CORE-LE [11].

This paper presents the physical-mathematical and numerical formulation of the non-isothermal multiphase flow and reactive transport. There is a description of the general characteristics of the FADES-CORE code which allows for the solution of additional thermal-hydro-geochemical and mechanical problems. The potential of this code has been illustrated by modeling a test for hydration and heating of a thermohydraulic cell carried out by CIEMAT within the FEBEX project. Lastly, we discuss the possibility of using this code to solve other types of problems.

2 THERMO-HYDRO-GEOCHEMICAL CONCEPTUAL MODEL

The porous medium is considered to be comprised of a liquid phase made up of the species water and dissolved air, a gas phase consisting of vapor and “dry” air (a fictitious species which encompasses all the chemical species that make up air except vapor) and a solid phase, consisting of different mineral phases.

Water flows throw a porous medium in liquid form in response to the hydraulic gradient (Darcy’s Law), and in the form of vapor, both in response to the humidity gradient (Fick’s Law) as well as in a convective form related to the movement of air over the land.

Water flows in vapor and liquid form interact through evaporation and condensation. When a liquid front invades a very dry area, part of it evaporates. In contrast, if there is a drop in temperature or in the pressure of the liquid, part of the water vapor will condense. The transition of water from vapor to liquid form and vice-versa takes place with a high degree of energy exchange (585 cal/g for water at 20 ºC), which means that the energy transported in the medium comes primarily from the change in the water phase. An analysis of the multiphase
flow must take the following processes into account [10], [14]: a) water flow in liquid form (advection), b) water flow in vapor form (advection and diffusion), c) air flow in the gas phase (advection and diffusion), d) air flow dissolved in water (advection), e) heat flow through a solid matrix (conduction), f) heat flow through the liquid (convection) and g) heat flow in the gas phase (convection).

Each of these processes is governed by a conservation equation. These equations, in turn, are linked together due to exchange relationships (phase changes, transport of heat between phases, etc.). The following equilibrium relationships are commonly assumed [10], [14]: a) equilibrium between the liquid phase and the vapor phase (Kelvin’s or the psychrometric equation, b) thermal equilibrium among the three phases, c) equilibrium between the air in dissolution and the air in the gas phase, d) equilibrium between the dissolved air in the liquid and the liquid (Henry’s Law) and e) the equilibrium between the air that is part of the gas and the vapor (Dalton’s Law).

The mechanisms of physical transport are [14]: a) advection, b) molecular diffusion and c) mechanical dispersion. Each of these processes yields a solute mass flow per medium surface unit and per unit of time. The solutes may also undergo radioactive decay processes, and become part of other species.

The chemical interaction processes include both homogeneous and heterogeneous reactions [9], [11]. The homogeneous reactions entail complexation, acid-base and redox reactions. The heterogeneous reactions are: cation exchange, mineral dissolution-precipitation, gas dissolution-exolution and adsorption reactions.

The balance of the i-th species (water, air, heat if it is considered to be another species, or the solute) may be generally formulated by means of the following expression:

\[
\frac{\partial m_i}{\partial t} = -\nabla \cdot \mathbf{q}_{\text{tot}}^i + r_i^i
\]

where \(m_i\) is species mass \(i\) per unit of the volume of the porous media (control volume), \(\mathbf{q}_{\text{tot}}^i\) the total mass flow of species \(i\) (advective flow and diffusive flow) and \(r_i^i\) is the term source/sink (mass which is added/removed per unit of time and media volume). Equation (1) applied to the species water, air, heat and the i-th solute adhere, respectively, to the following expressions:

\[
\frac{\partial}{\partial t} \left( \phi_S l_i^w X_l^w + \phi_S g^w X_g^w \right) = -\nabla \cdot \left( \rho_l X_l^w \mathbf{q}_l + \rho_g X_g^w \mathbf{q}_g + \mathbf{j}_g^w \right) + r_w^w
\]
\[ \frac{\partial \left( \phi \left( \rho \frac{\partial X^a}{\partial t} + \rho \frac{\partial X^a}{\partial t} \right) \right)}{\partial t} = -\nabla \cdot \left( \rho \frac{\partial X^a}{\partial t} + \rho \frac{\partial X^a}{\partial t} + j^a \right) + r^a \tag{3} \]

\[ \frac{\partial}{\partial t} \left( \rho (1-\phi) h + \sum_{k=1}^{N_{FM}} \left( \phi S_k \rho_k h_k \right) \right) = -\nabla \cdot \left[ \Lambda \nabla T + \sum_{k=1}^{N_{FM}} h_k \rho_k q_k + \sum_{k=1}^{N_{FM}} \sum_{j=1}^{N_k} \sum_{i=1}^{j} h_i^j \right] + r^q \tag{4} \]

\[ \rho_j X^i_j \theta_j \frac{\partial C_j}{\partial t} + \frac{\partial (\rho_j X^i_j \theta_j P_j)}{\partial t} = \frac{\partial (\rho_j X^i_j \theta_j W_j)}{\partial t} + \frac{\partial (\rho_j X^i_j \theta_j Y_j)}{\partial t} = L^s(C_j) + \rho_j \sum_{k=1}^{N_k} \lambda_{kj} C_k + r_j \left( C_j^0 - C_j \right) \tag{5} \]

with \( L^s(\cdot) = \nabla \cdot (\rho_j X^i_j \theta_j D^j(\nabla \cdot \cdot)) - \rho_j X^i_j q_j \nabla (\cdot) + (r_e - r_c \cdot \cdot) - \rho_j X^i_j \theta_j (\cdot) \sum_{i=j+1}^{N_k} \lambda_{ji} \) and where the sub-indices \( l, g, k, r \) and \( j \) indicate the liquid phase, gas phase, \( k \) phase, solid phase and \( j \)-th solute, respectively. \( S_k, \rho_k, \theta_k, q_k \) and \( h_k \) are the degree of saturation, density, and volumetric content, the advective flow and specific enthalpy of the \( k \) phase, respectively. \( T \) is the temperature, \( \Lambda \) is the mean thermal conductivity of the porous media, \( \theta_j \) is the diffusive flow of the \( i \)-th species in the \( k \) phase and \( X^i_k \) is the mass fraction of the \( k \) phase. \( N_{FM} \) is the number of mobile phases, \( t^s, r^s, r^q \) are the terms source/sink of water, air, and heat respectively. \( r_e \) and \( r_c \) are the condensation and evaporation rates, respectively. \( C_j, P_j, W_j, \) and \( Y_j \) are the total dissolved, precipitated, exchanged and adsorbed concentrations of species \( j \), respectively. \( C_j^0 \) is the external concentration of the \( j \)-th solute in the inflowing water, \( \phi \) is the porosity, \( D^j \) is the dispersion tensor of the \( j \)-th solute and \( \lambda_{kji} \) is the constant of radioactive decay of the \( k \)-th species and \( j \)-th species.

### 3 NUMERICAL MODEL

The general equation (1) of the balance of the mass of any species may be written as follows:

\[ L \left(m^i, q^i_{\text{tot}} \right) = -\nabla \cdot q^i_{\text{tot}} + \gamma^i - \frac{\partial m^i}{\partial t} = 0 \tag{6} \]

so that balance \( L \left(m^i, q^i_{\text{tot}} \right) \) is null for the exact solution. If the exact solution in (6) is
substituted by the numerically computed solution \( (m')^N, (q_{tot}')^N \), then it is found that \( L((m')^N, (q_{tot}')^N) \) is not null as it is an approximate solution. Therefore, in order to integrate Equation (6) into a given domain \( D \), the mean weighted error obtained in (1) must be null when the numerical solution is used (the method of finite elements of Bubnov-Galerkin), so that

\[
\int_D L((m')^N, (q_{tot}')^N) \xi(x) dx = 0
\]

where \( \xi(x) \) are the form functions or weighting functions. If expression (6) is replaced by \( L( \) and Green’s theorems are applied, the result is a weak formulation, where the independent variables chosen are gas pressures \( P_g \), liquid pressures \( P_l \), temperatures \( T \) and the total concentrations \( C_i \) of the chemical species for each of the mass balance equations.

After the application of Green’s theorems, the spatial integration into the domain of Equation (7) is carried out by weighting the value of the sub-integral functions at several Gauss points in the domain, so that for a generic function \( f(x) \) it would hold that

\[
\int_D f(x) dx = \sum_{i=1}^{npg} w_i f(x_i)
\]

where \( npg \) is the number of Gauss points, \( w_i \) is the weight related to the \( i \)-th Gauss point and \( f(x_i) \) is the value of the function at point \( i \).

In order to integrate the temporal derivatives, a mass conservative technique is applied [5], [10]:

\[
\int_{t_k}^{t_{k+1}} \frac{\partial (m_i')^N}{\partial t} dt = \left[ (m_i')^N \right]_{k+1}^{k} - \left[ (m_i')^N \right]^k
\]

where \( \left[ (m_i')^N \right]_{k+1} \) and \( \left[ (m_i')^N \right]^k \) is the mass of species \( i \) in time \( k+1 \) and \( k \), respectively.

In this way, if (8) is applied to each of the integrals in which (7) is decomposed and taking (9) into account, the result is an equation system determined by the following expression:
\[ A^i \dot{x}^i + B^i \frac{dx^i}{dt} = g^i \]  

(10)

where \( i = \text{water, air, temperature} \) and \( \text{solute } i \) with \( i = 1, \ldots N_C \); \( A^i, B^i \) are the squared matrices of \( NN \times NN \) of size, symbolizing the coefficient matrix of the unknown variables \( x^i \), which are : \( P_l \) (liquid pressure), \( P_g \) (gas pressure), \( T \) (temperature) and \( C_i \). \( g^i \) is the vector of independent terms and \( N_C \) is the number of primary species in dissolution.

In general, the linear approach to the solution will not fulfill the balance of mass,

\[ r(t) = L(x^*) \neq 0 \]  

(11)

If the fulfillment of (11) is waived, then each time increment using method SS11 [1], [2] will result in:

\[ s_j = \int_{t_{j-1}}^{t_j} w(t) r(t) dt = 0 \]  

(12)

where \( w(t) \) is a function of weight indicating the importance assigned to the fulfillment of the system at each instant of the interval and \( s_j \) is the mean residual at time \( t \). Another way of defining the mean residual is by using Newmark’s generalized method. GN11 [3]

\[ s_j = r(m_j) = r(x^*(m_j)) = r((1 - m)x_{j-1} + m x_j) \]  

(13)

with

\[ m = \frac{tm_j - t_{j-1}}{t_j - t_{j-1}} \]  

(14)

where \( tm_j \) is a mean time of time increment \( j \) where the fulfillment of (11) is required.

If Equation (12) is applied to Equation (10) and using Simpson’s quadrature, the following is obtained for each species \( i \):

\[ s_j^i = \sum_{k=1}^{3} w_k \left( A^i k x_k^i \Delta t + B^i k (x_j^i - x_{j-1}^i) - g^i \Delta t \right) = 0 \]  

(15)

where \( x_{j-1}^i \) are the values of the variables at the instant before and these values are known.
The unknown variables are $x^j_i$.

The system of equations (15) applied to each species (water, air, energy and solutes) can be solved by using two schemes: a “monolithic” scheme, which consists of jointly solving all of the equations, or, depending on the degree of coupling between the flow and transport processes, the solution may be found by adopting a “staggered” scheme. The latter consists of first solving the equations coupled to the flow of liquid, gas and energy and then, solving the equation for the transport of reactive solutes. The application of monolithic schemes requires a greater amount of computation work, since all of the equations are solved simultaneously. Here the staggered scheme has been used for the following reasons:

a) The model applied was satisfactory to dissolutions having low concentrations.

b) Solutes present in the water have an effect on its density and viscosity, which, in principle, could change the water flow. However, for high concentrations of 40 gr/kg the water density rarely varies as little as 2.5% and the viscosity varies around 0.3%, which would not justify an important enough coupling between flow and transport to warrant the use of a monolithic scheme. As this dependency is testimonial, it is more efficient to adopt “staggered” schemes, thereby saving an enormous amount of computation work.

On the other hand, since the dissolutions are not very concentrated, the Debye-Hückel equations hold true for the calculation of the activity coefficients and the ideal conditions for the dissolutions. For the Debye-Hückel equations to hold true, the maximum value of ionic strength is approximately 0.7, or the equivalent of maximum concentrations for salts such as sodium chloride of 40 gr/kg of solute in dissolution. The opposite case would not only be useless for the geochemical model, but would also be inapplicable to the flow model.

The properties of the water are more dependent on the temperature than on solute concentration, within the range of values used by the model, which are restricted by the fulfillment of the Debye-Hückel formulation.

Even so, it is possible to use an iterative resolution scheme by means of which the flow equations of liquid, gas and energy are solved first. Later, the transport equation of the reactive solutes is determined and the concentrations that were calculated are verified to see whether or not they bring about changes in the water density, so that if they surpass a defined tolerance, the flow is calculated again with the new density value.

### 4 DESCRIPTION OF THE CODE

The _FADES-CORE_ code allows us to model the nonisothermal multiphase flow and the transport of one and two-dimensional reactive solutes. It also allows us to solve three-dimensional problems with axial symmetry. The elements implemented in the code are 1-D
linear and non-linear elements, triangles and quadrilaterals with different integration points. The processes that have been taken into account are those which are described in the conceptual model.

The flow is solved in terms of liquid pressure and gas pressure. Heat transport is solved in terms of temperature. Both multiphase flow and heat transport are solved in a coordinated way, which implies solving a non-linear problem that satisfy (15). To this end, the Newton-Raphson method was applied. Thanks to the use of the mass conservation technique, secondary derivatives with respect to the independent variables are not introduced, which provides greater speed in calculating the application of the Newton-Raphson method [5], [10].

After the flow has been solved, the iterative transport of reactive species is solved. To do so, the Darcy velocities and the evaporation/condensation ratios are calculated, and the mechanical dispersion and molecular diffusion coefficients are evaluated. There will be as many transport equations as there are primary chemical species. The transport equations are solved in terms of concentrations of the species defined as primary. After these have been obtained, the node-to-node chemical system by means of the Newton-Raphson method is solved and the chemical source/sink term of the transport equation is obtained. To do this, it is necessary to calculate the balance constants in order to obtain the set of reactions between primary species, the calculation of activity coefficients and their derivatives with respect to the primary species, the calculation of the quantity of dissolved/precipitated mineral and of the quantity of solute adsorbed/desorbed, and the updating of the primary and secondary species and the adsorbed and dissolved species at each period in time [9].

Therefore, the transport equation is solved once more, taking this term into account (sequential iteration method). The process is repeated until the transport convergence criterion which will have been established is met. The chemical source/drain term of the transport equation represents the mass transferred between the aqueous phase and other phases (through dissolution/precipitation, exchange and adsorption processes). In order to obtain such a term, when looking at the chemical equations, a highly non-linear problem must be solved. The geochemical system is solved along with the transport equations by means of an iterative process and different schemes can be applied: completely iterative scheme, partially iterative scheme, in which it will only be iterated in those nodes where the chemical conditions do not meet tolerance criteria, and non-iterative scheme. The choice of the primary chemical species basis should be carefully considered and will be calculated by solving the transport of the system of differential equations and the secondary chemical species, calculated using the chemical reactions between primary species equations.

After reactive species transport has been solved (Figure 1), the liquid density variation can be evaluated as its composition changes, liquid density varying with the concentrations of the dissolved species. If the variation is greater than 2% the flow is once again solved in order to then solve reactive solute transport. Repetition is not usually necessary, as the solutions are
diluted and influence on the density of the liquid is minimal. In fact, for concentrations higher than saline content in the sea, the hypotheses used for flow, species transport and chemical reactions are not valid.

A convergence criteria is usually established on the balance of mass and the values of the unknown variables in absolute and relative terms. In absolute terms, it implies that the values obtained from a certain iteration of the remainder are lower than a defined maximum, both in the balance of mass and in the unknown variables. In relative terms, a maximum is set in respect to mass variation, for the balance of mass, and a maximum is also set in terms of the variable of state given, for the unknown variable of the problem.

The code incorporates an automatic algorithm for generating the time intervals of the FADES program [10]. The organization of the time periods between the times of duration of the different stages into which a process can be divided is carried out within the code. When an observation time is reached, the result is stored in the corresponding files. The automatic algorithm of a time period calculates the optimum time, in terms of the convergence behavior of the process so that when the process shows no important variations in the variables, this time period will be increased. When there are problems of convergence, because the variables change quickly, it will be decreased. Optimization criteria is related to the convergence of the remainder and of the variables of state. In order for a determined time period to achieve convergence, convergence must also be reached in the solving of the chemical system, the

**Figure 1.** Chart describing how FADES-CORE works
transport system and the non-isothermal multiphase flow, in this order.

5 APPLICATION

In the example we are going to look at now, we have taken as a model non-isothermal multiphase flow and the reactive transport of heating and hydration experiment of the CT-23 thermo-hydraulic cell, carried out by CIEMAT, in samples of compressed bentonite in order to characterize the geo-chemical procedures induced by the combined effect of a thermal gradient and a water flow [14].

The experiment consisted of subjecting a sample of compressed bentonite in an airtight cell heated on the top exterior side and hydrated on the opposite side for 4394 hours. The cell was then taken apart and the water was extracted from the layers in which the bentonite sample had been cut.

The model taken is one-dimensional with the longitudinal axis of the cell as an X-axis representing the results obtained. The heater is placed to the right of the axis and the hydration source to the left. The thermo-hydraulic model has been calibrated taking into account the fact that the total volume of inflowing water is known (486 cm³). Therefore, the initial gravimetric water content is 11.23%. In order to adapt the water contents at the end of the test in the layers near the heater the intrinsic permeability of the liquid and gas was changed. After the cell was set up, the outer side was heated first, reaching a temperature of 100 ºC (boundary condition of the upper end over 100 ºC). On the lower side, water was introduced at a pressure of 1000 kPa without letting the gas out. The gas was at atmospheric pressure and an initial temperature of 20 ºC. The test was carried out over 4394 hours. In figures 2 and 3, the gravimetric water content at the end of the test and the evolution of water introduction are shown.

Figure 4 shows the results of the spatial distributions of sodium provided by the model at different times. In this diagram, in the x-axis, dimensionless distances are shown. We can see an important increase in concentration in areas near the heater (to the right of the x-axis) due to evaporation processes, as well as a notable dilution in areas near the hydration source (origin of coordinates) due to the introduction of distilled water. Half way through the test, the sodium concentration tends to decrease progressively near the heater as a consequence of the diffusion phenomenon and the arrival of the hydration source.
Figure 2. Final humidity content. The values measured and those calculated in the different layers.

Figure 3. Inflow of water.
5 CONCLUSIONS

In this paper, we have presented the numerical formulation of nonisothermal multiphase flow with reactive transport and the description of the FADES-CORE code implemented as well as an example of validation, by which some of the code's capabilities are shown. The model developed from the thermohydration test carried out and the geochemical model accurately reproduce the most reliable experimental results observed; given the complexity of the model and the lack of knowledge as to some of the parameters, both thermohydraulic or geochemical, which served to calibrate the water inflow, the end humidity distributions and the end chemical species distributions.

The program developed efficiently resolves any combination of flows and reactive transport: Problems related to conservative transport, flow, energy transport or chemical speciation can be solved. One-dimensional, two-dimensional and axisymmetric problems can be analyzed.

The possibility that there may be variations in the boundary conditions over time has been taken into consideration, and several time steps may be defined whereby it is possible to select the times during which one needs to have the information related to variables, parameters and

Figure 4. Spatial distribution of sodium dissolved at different times.
flows. The time steps are calculated automatically depending on the convergence conditions of the problem being solved. FADES-CORE is able to reproduce the inflows of water, the final damp spots, the final distributions of temperature, the concentrations of the dissolved species, precipitated minerals, exchange cations and adsorbed species.

As regards the numerical model used, the equations were solved numerically by means of the Bubnov-Galerkin method. For the temporal discretization of the solute transport equations, seven different techniques may be used. It is possible to employ one-dimensional and two-dimensional elements (triangles or rectangles) that may be linear or quadratic in terms of integration.

FADES-CORE has been thoroughly checked with analytical solutions, and as far as possible, with other codes. This verification guarantees that it will work accurately.

The code was able to be applied to real cases. The modeling of the heat and hydration test carried out in the thermal-hydraulic cell CT23 proves that it is necessary to consider the phenomena of evaporation and condensation both in the flow and transport of solutes. Therefore, the THG simulation of this experiment would entail the consideration of a reactive transport and multiphase flow model.

The code has been applied to determine the thermo-hydro-geochemical behavior of clayey porous media under different flow and heat conditions, as well as the application presented in this paper, although it may also be extended to any porous media such as, concrete and asphalt mixtures, for example.

ACKNOWLEDGEMENTS

This research was carried out under the FEBEX project and funded by ENRESA through a Marco Agreement with the University of La Coruña and the Foundation of Civil Engineering of Galicia (FEBEX Project, code 703231). The overall Project is part of a Project funded by the European Commission (Project F14W-CT95-006 of the Nuclear Fission Program). The laboratory tests were carried out by CIEMAT. Part of the research was also done under Project CICYT HID98-282.

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