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Reactive Transport of CO2 in Saline Aquifers with implicit geomechanical analysis

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Abstract

Geological storage of CO_2 in saline aquifers is a promising way to reduce the concentration of the greenhouse gas in the atmosphere. Injection of CO_2 will, however, lead to dissolution of minerals in regions of lowered pH and precipitation of minerals from transported ions in regions of higher pH. The geomechanical implications of these changes on the stability of the reservoir are of crucial importance in the evaluation of potential injection reservoirs. The possible injection rate for given over-pressures of the injected CO_2 depends on the porosity and permeability of the rock matrix in the vicinity of the injection well. Local fracturing in this region can be a tool for increasing the injection flow rate but a geomechanical analysis will be needed in order to make sure that this fracturing will not affect the geomechanical stability outside this limited region to a significant degree. This paper presents a new rewritten version of RetrasoCodeBright (RCB) which have been extended to simulations of CO_2 storage in saline aquifers. An advantage of this code compared to other codes is the *implicit* geo-mechanical module. The code has been rewritten to account for non-ideal gas through corrections of gas density and gas solubility in all transport terms. Newton-Raphson method used to solve the flow and mechanics in RCB has been improved so as to improve convergence even under high gas injecting pressures. A 2D hydro-chemical-mechanical problem is used to illustrate the modified RCB code.

1.   Introduction

The geological storage of greenhouse gas in deep saline aquifers can be one of the most promising options to reduce the concentration of CO2, the major greenhouse effect contributor, in the atmosphere (Haszeldine, 2004). Saline aquifers are water bearing porous layers of sandstone or limestone in the subsurface and by far they are the volumetrically largest, and widespread, proposition for large-scale CO2 storage.   Currently there are four

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functioning CO2 sequestration projects in the world; two in Norway, one in Algeria, and one in Canada. For sure more projects and relative research work will be carried out in the close future to meet the strong needs of reducing greenhouse gas emissions.

1.1   The numerical tool RCB

The simulation model that predicts the movements of CO2 after injection in the reservoir is the essential part of the scientific program. The goals of numerical modelling and simulation will address three important issues associated with subsurface CO2 storage plans for all the injection projects. Firstly simulations are allowed to have *what-if* scenarios by using the data from the injection site. Secondly simulations can reveal the ultimate fate of injected CO2 in the reservoir in terms of pressure evolution, phase evolution, chemical reactions, and their influence in porosity, permeability evolution, and geomechanical evolution in the whole vicinity. Thirdly numerical modelling is an important tool for risk assessment considering the integrity with caprock and safety questions about the high density CO2 fluid invades into other formations and/or deleted oil/gas wells (CO2SINK). At present there is no universal modelling tool that can simulate the complex, coupled temperature- and pressure-dependent process of multi-component, multiphase fluid flow in the subsurface and the chemical water-rock interactions and phase changes that accompany these movements.

The time scale for evaluation of storage safety vary worldwide but a number of 10000 years frequently pop up in the discussion of long term storage safety. These long time scales challenge our current level of understanding of the whole storage system, which involves implicit couplings between fluid flow, reactions and potential implications for geomechanical stability. Most of the reservoir simulators used for studies of CO2 storage up to now have been based on finite volume algorithms and there are correspondingly no implicit bridges to the geo-mechanical analyses. Recently some of these simulators have been extended with a finite element library which enables external couplings to geo-mechanical analysis tools. Whether these explicit couplings are satisfactory in terms of capturing the dynamic coupling between the reactive transport and the corresponding geo-mechanical implications remains unverified.

In view of the discussion above it is desirable to develop a reservoir simulator which has implicit coupling between reactive flow and the geo-mechanical analysis. In the work presented here code RCB (RetrasoCodeBright) has been chosen as the software platform. RCB is the result of coupling two codes: CodeBright and Retraso. CodeBright (COupled DEformation of BRIne Gas and Heat Transport) was designed for the thermo-hydraulic-mechanical analysis of three-dimensional multiphase saline media (Olivella et al., 1996). In other words, CODE-BRIGHT permits the modeling of deformation, mechanical processes and heat transport in multiphase. Retraso (REactive TRAnsport of SOlutes) is a code for solving reactive transport problems (Saaltink et al., 1997). The design of implicit coupling between Retraso and CodeBright makes the code RCB perfect for CO2 injection calculations.

Basically in one time step, which is pre-described by user, CodeBright module first calculates the flow properties, heat transport and geomechanical deformation, then copy all the variables including independent variables, meaning liquid pressure (Pl), gas pressure (Pg), temperature (T) and deformation (u), and dependent variables, like flux of liquid, flux of gas, hydraulic saturation, porosity that will be solved in reactive transport calculations to Retraso module. Retraso module updates all the flow properties by solving the matrix of concentrations of primary species and secondary species. When calculations in Retraso part are successfully finished, Retraso module passes all the variables that have been taken part in chemical calculation to CodeBright module to get ready for the next time step. By now the calculations for one time step is completely finished. Both CodeBright module and Retraso module adopt Newton-Raphson iteration method to solve the matrices made up of the governing equations which will be elaborated later. Figure 1 schematically illustrates this process.

1.2   Governing equations in CodeBright module

The governing equations for non-isothermal multiphase flow of water and gas through porous deformable saline media have been presented by Olivella et al. (1994). These equations can be categorized into four main groups, which are balance equations, constitutive equations, equilibrium relationships and definition constraints.
Equations for mass balance were established following the compositional approach. That is, mass balance is performed for water, gas and salt species instead of using solid, liquid and gas phases. Equation for balance of

energy is established for the medium as a whole. The equation of momentum balance for the porous medium is reduced to that of stress equilibrium.

Mass balance of solid

$$\frac{\partial}{\partial t}(\theta_s(1-\phi)) + \nabla \cdot (j_s) = 0 \tag{1}$$

where θ_s is the mass of solid per unit volume of solid, j_s is the flux of solid and ϕ is porosity. From this equation, an expression for porosity variation is obtained as:

$$\frac{D_s\phi}{Dt} = \frac{1}{\theta_s}[(1-\phi)\frac{D_s\theta_s}{Dt}] + (1-\phi)\nabla \cdot \frac{du}{dt} \tag{2}$$

where u is solid displacements.

Mass balance of water

$$\frac{\partial}{\partial t}(\theta_l^w S_l\phi + \theta_g^w S_g\phi) + \nabla \cdot (j_l^w + j_g^w) = f^w \tag{3}$$

where θ_l^w and θ_g^w are respectively water in liquid and gas phase, *Sl, Sg* is degree of saturation of liquid and gaseous phases i.e., fraction of pore volume occupied by each phase, f^w is the external supply of water.

Mass balance of gas

$$\phi \frac{D_s(\theta_l^a S_l + \theta_g^a S_g)}{Dt} + (\theta_l^a S_l + \theta_g^a S_g)\frac{D_s\phi}{Dt} + ((\theta_l^a S_l + \theta_g^a S_g)\phi)\nabla \cdot \frac{du}{dt} + \nabla \cdot (j_l^{'a} + j_g^{'a}) = f^a \tag{4}$$

where θ_l^a and θ_g^a are respectively mass of gas in liquid phase and gaseous phase, $j_l^{'a}$ and $j_g^{'a}$ are total mass flux of gas in liquid phase and gaseous phase relative to the solid phase, and f^a is gas supply.

Momentum balance of the medium

The momentum balance reduces to the equilibrium of stresses if the inertial terms are neglected:

$$\nabla \cdot \sigma + b = 0 \tag{5}$$

where σ is stress tensor and b is the vector of body force.

Internal energy balance of the medium

The equation for internal energy balance for the porous medium is established taking into account the internal energy in each phase (*Es, El, Eg*):

$$\frac{\partial}{\partial t}(E_s\rho_s(1-\phi) + E_l\rho_l S_l\phi + E_g\rho_g S_g\phi) + \nabla \cdot (i_c + j_{Es} + j_{El} + j_{Eg}) = f^Q \tag{6}$$

where i_c is energy flux due to conduction through the porous medium, the other fluxes (j_{Es}, j_{El}, j_{Eg}) are advective fluxes of energy caused by mass motions and f^Q is an internal/external energy supply. In this case this term accounts, for instance, energy dissipation due to medium deformation which is not explicit because it is negligible in most cases. The use of the material derivative allows obtaining an equation formally similar to the mass balance of water. The reason for the similarity is that both water and internal energy are considered present in the three phases.

Constitutive equations and equilibrium restrictions

Associated with this formulation there is a set of necessary constitutive and equilibrium laws. Table 1 is a summary of the constitutive laws and equilibrium restrictions that should be incorporated in the general formulation. The dependent variables that are computed using each of the laws are also included.
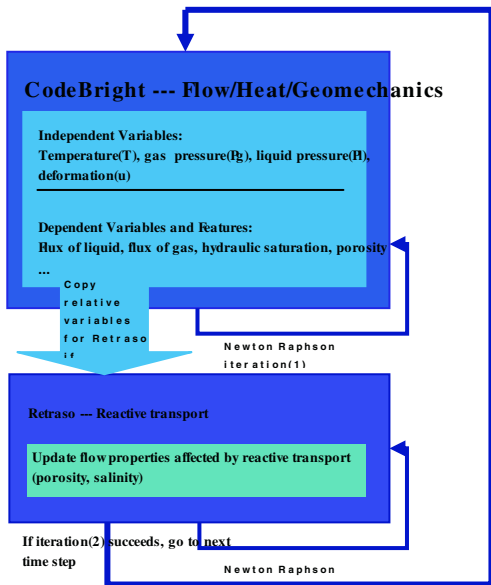
Fig 1 RCB solves the integrated equations sequentially in one time step.

Constitutive equations	Variable name	variable
Darcy's law	Liquid and gas advective flux	q_l, q_g
Fick's law	Vapour and gas non-advective flux	i_g^w, i_l^a
Fourier's law	Conductive heat flux	i_c
Retention curve	Liquid phase degree of saturation	S_l, S_g
Mechanical constitutive model	Stress tensor	σ
Phase density	Liquid density	ρ_l
Gas law	Gas density	ρ_g
Equilibrium restrictions	Variable name	variable
Henry's law	Air dissolved mass fraction	ω_l^h
Psychometric law	Vapour mass fraction	ω_g^w

Table 1 Constitutive equations and equilibrium restrictions

The independent variables

The governing equations for non-isothermal multiphase flow of liquid and gas through porous deformable saline media have been established. Variables and corresponding equations are tabulated as the following:

Equation	Variable name	Variable
Equilibrium of stresses	Displacements	u
Balance of liquid mass	Liquid pressure	Pl
Balance of gas mass	Gas pressure	Pg
Balance of internal energy	Temperature	T

Table2. Equations and independent variables

After the spatial discretization of the partial differential equations, the residuals that are obtained can be written (for one finite element) as:

$$
\begin{pmatrix} r_u \\ r_{Pl} \\ r_{Pg} \\ r_T \end{pmatrix} = \frac{d}{dt}\begin{pmatrix} d_u \\ d_{Pl} \\ d_{Pg} \\ d_T \end{pmatrix} + \begin{pmatrix} a_u \\ a_{Pl} \\ a_{Pg} \\ a_T \end{pmatrix} + \begin{pmatrix} b_u \\ b_{Pl} \\ b_{Pg} \\ b_T \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}
\tag{7}
$$

where **r** are the residuals, $d\mathbf{d}/dt$ are the storage or accumulation terms, **a** are the conductance terms, and **b** are the sink/source terms and boundary conditions. After time discretization a more compact form can read as:

$$
r\left(X^{k+1}\right) = \frac{d^{k+1} - d^k}{\Delta t^k} + A\left(X^{k+\varepsilon}\right)X^{k+\theta} + b\left(X^{k+\theta}\right) = 0
\tag{8}
$$

where *k* is the time step index, : **X**=[(ux,uy,uz,Pl,Pg,T)(1), ..., (ux,uy,uz,Pl,Pg,T)(n)], is the vector of unknowns (i.e. a maximum of seven degrees of freedom per node), **A** represents the conductance matrix. The Newton-Raphson scheme of solution for this non-linear system of AE's is:

$$
\frac{\partial r\left(X^{k+1}\right)}{\partial X^{k+1}}\left(X^{k+1,l+1} - X^{k+1,l}\right) = -R\left(X^{k+1,l}\right)
\tag{9}
$$

where l indicates iteration. In the present approach, the standard Galerkin method is used with some variations in order to facilitate computations.

The mathematical equations for the system are highly non-linear and they will be solved numerically. The numerical approach can be viewed as divided into two parts: spatial and temporal discretizations. Finite element method is used for the spatial discretization while finite differences are used for the temporal discretization. The discretization in time is linear and the implicit scheme uses two intermediate points, $t^{k+\varepsilon}$ and $t^{k+\theta}$ between the initial t^k and final t^{k+1} times. The Newton-Raphson method is adopted to find an iterative scheme. This scheme has been modified through the introduction of a relaxation factor approach according to the algorithms of Nakata and Fujiwara (1993), in which we obtain the proper relaxation factors by combining the general tendency method (Nakata and Fujiwara, 1993) and time step reduction method.

1.3 Reactive transport in Retraso

The Retraso part of the code has a built in state of the art geochemical solver and in addition capabilities of treating aqueous complexiation (including redox reactions) and adsorption. The density of CO_2 plumes which cumulate under traps of low permeability shale or soft clay depends on depth and local temperature in each unique storage scenario. The difference in density and the density of the groundwater results in a buoyancy force for penetration of CO_2 into the cap rock. And even if the solubility of water into CO_2 is small dissolution of water into CO_2 may also lead to out-drying. Mineral reactions between CO_2 and shale minerals are additional effects which eventually may lead to out-drying and embrittlement. Linear geo-mechanics may not be appropriate for these effects. In particular clay is expected to exhibit elastic non-linear contributions to the geo-mechanical properties. Different types of non-linear models are already implemented in the CodeBright part of the code and the structure of the code makes it easy to implement new models derived from theory and experiments.

In the current version we have extended the code from ideal gas to handling of CO_2 according to the SRK equation of state (Soave, 1972). This equation of state is used for density calculations as well as the necessary calculations of fugasities for the CO_2 phase as needed in the calculation of dissolution of CO_2 into the groundwater. See also Hellevang & Kvamme (2007) for more details. Other alternative equations of state can easily be implemented to replace SRK. The dissolution and precipitation of minerals in CO_2 injection scenarios are slow natural processes, where the kinetic law (Lasaga et al., 1994) is applied in RCB. The mathematical equations for the system are highly non-linear and are solved numerically (Saaltink et al., 2004). All kinetic parameters for the systems in this study was collected from Mucci and Morse (1983).

2. Simplified model system

In lack of real field data for relevant systems with significant reactivity we present one example from a simplified model. A 2D example is made up with gravity acceleration equal to -9.81, working on Y direction. Figure 2 schematically shows the vertical profile of this 2D example which lies 1000m under ground in X-Z plane. It is 1000m long in X direction and 200m high in Z direction where injection formation which consists of homogenous aquifer is 150m high and caprock is 50m high. CO_2 will be injected in the right-down corner. The material properties are given in Table 3 and correspond to sandstone aquifers mainly calcite with a caprock mainly quartz. Tab4 shows the initial and boundary conditions, and Tab5 shows the chemical species.

The method for specifying the primary and secondary species is based on that devised by Peter Lichtner for the code MPATH and used by Carl Steefel for the code 1DREACT (Steefel, 1993). The code RCB requires the user to specify a set of aqueous primary species (or component species) to determine the number of independent components of the system. The choice of aqueous primary species is not unique, and the set of most abundant species for each component is recommended to avoid numerical problems. The calculation of volume fraction and surface reactive area of calcite and quartz in the whole formation is adapted according to the paper by S.P.White (2002). Kinetic geochemical reactions are assumed for all fluid-mineral reactions.
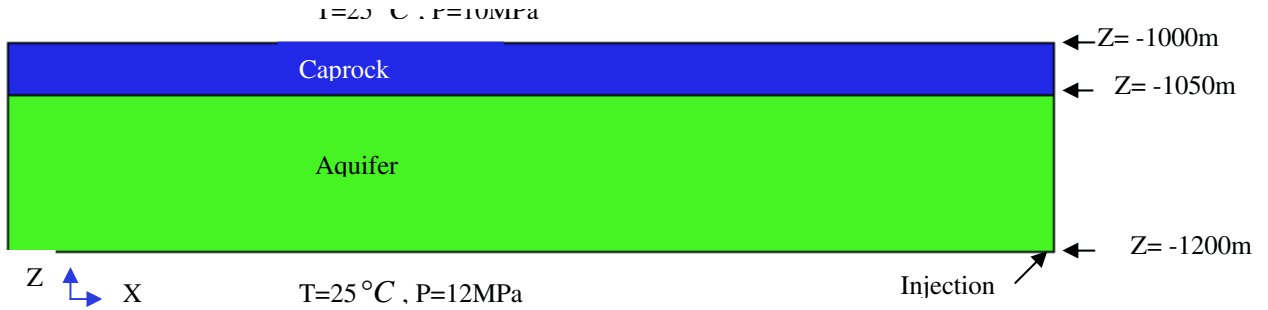
T=25°C . P=10MPa

Caprock   ← Z= -1000m

                                                                           ← Z= -1050m

Aquifer

                                                                           ← Z= -1200m

Z ↑ → X   T=25 °C , P=12MPa   Injection

Fig 2 Vertical profile of the finite difference model with rock units

Property	Caprock	Aquifer
Young's modulus, E(GPa)	0.3	0.3
Poisson's ratio, v(-)	0.2	0.2
Saturated rock density, $\rho_s (kg/m^3)$	2.26	2.26
Zero stress porosity, ϕ_0 (-)	0.1	0.2
Zero stress permeability, $k_0 (m^2)$	1.0e-15	1.0e-13
Irreducible gas saturation, S_{rg} (-)	0	0
Irreducible liquid saturation, S_{rl} (-)	0.3	0.3
Van Genuchten's gas-entry pressure, P_0 (kPa), (at zero stress)	196	19.6
Van Genuchten's exponent, m	0.457	0.457

Tab 3 Material properties

Parameter	Caprock	Aquifer
Pressure, P(MPa)	10-10.5	10.5-12
Mean Stress, σ (MPa)	22.28-23.39	23.61-26.49
CO2 injection pressure, P_o (MPa)	-	12.2
Gas and liquid outgoing pressure, P(MPa)	10	-

Tab 4 Initial and boundary conditions.
Values are given as a range because they vary with depth in each formation

Species	Caprock	Aquifer
Aqueous species	Ca^{+2}, HCO_3^-, H^+,SiO_2(aq)	Ca^{+2}, HCO_3^-, H^+,SiO_2(aq)
Mineral volume fraction	Calcite (0.1), Quartz(0.8)	Calcite(0.7), Quartz(0.1)
Mineral reactive surface	Calcite (100), Quartz(800)	Calcite (700), Quartz(100)
Gas	CO2	CO2

Tab 5 chemical species in different formations

3.   Results and discussion

Estimated gas pressure after 253 days of injection is plotted in fig. 3. Norm of gas phase flux is plotted in fig 4. Liquid saturations are plotted in fig. 5. The estimated principal stresses in xx and yy directions are plotted in figures 6a and 6b respectively. Positive direction for x is towards right and positive direction for y is upwards. Negative values for stress mean net stress opposite to these directions. Since this example is artificial we do not have any real measured material properties for which we could evaluate fracturing but the analyses will obviously be easier than an explicit analyse since the pressure and stress in given directions can be directly compared to experimentally measured breakdown pressures for a real system. For this specific example the low-permeable top results in estimated maximum horizontal stress towards the left end with a value of 23.8 MPa. The yy stress is lower than yy and for most regions lower than 4 MPa.
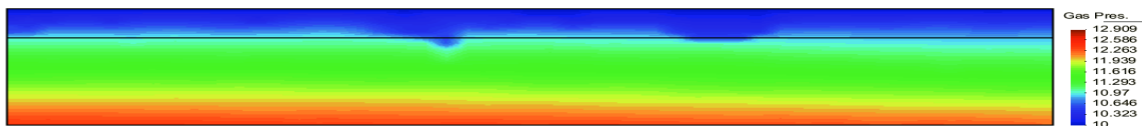

Fig 3 Simulated results of gas pressure (MPa) after 253 days of CO2 injection.

Fig 4 Simulated results of norm of gas phase flux (kg/s) after 253 days of CO2 injection
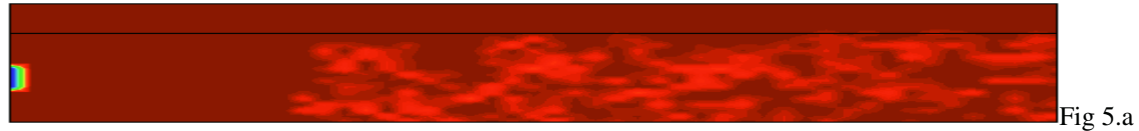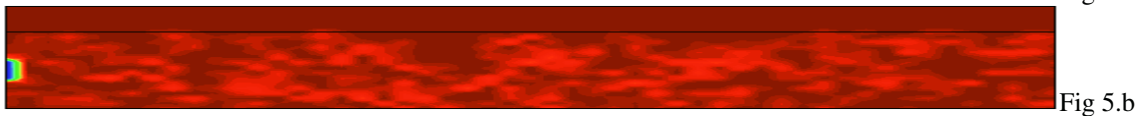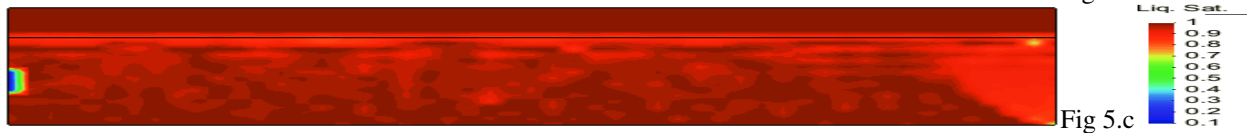

Fig 5.a

Fig 5.b

Fig 5.c

Fig 5 Simulated results of liquid saturation at the time points of 1day, 7days and 253days after CO2 injected.
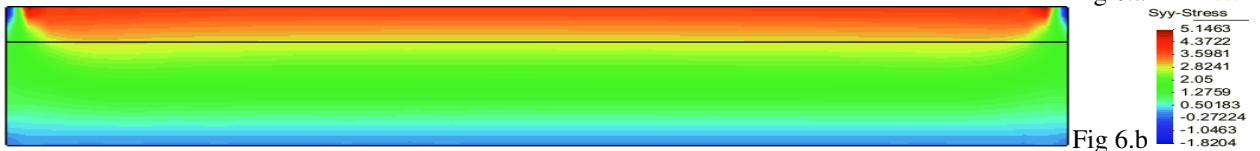

Fig 6.a

Fig 6.b

Fig 6 Simulated results of stress on XX direction (6.a) and YY direction (6.b) (MPa) at the time point253days after CO2 injected.
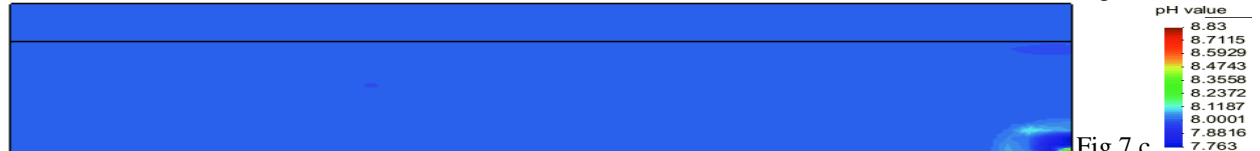

Fig 7.a

Fig 7.b

Fig 7.c

Fig 7 Simulated results of pH values at the time points of 26days, 133days and 253days after CO2 injected

4.   Conclusion

A new reservoir storage simulator for CO2 have been developed on the RetrasoCodeBright platform by inclusion of non-ideal gas description using an equation of state for calculation of gas solubility and incorporation of realistic

fluid densities as function of local pressures and temperatures. Numerical algorithms have also been modified so as to ensure converged solutions for the high pressures relevant for storage of CO2. A simple test case has been used to illustrate numerical solutions from the new CO2 simulator.

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