Simulating Long Term Reactive Transport of CO2 in Saline Aquifers with Improved code RCB

Shunping Liu, Bjorn Kvamme

***Abstract*—**The geological storage of CO2 in saline aquifers is believed to be one of the most promising ways to reduce the concentration of the greenhouse gas in the atmosphere. Injection of CO2 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 CO2 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 application of improved code RCB (RetrasoCodeBright) to simulate CO2 storage in saline aquifer. According to specification of carbon dioxide under injecting, gas density and gas solubility have been corrected in code RCB. Newton-Raphson method used to solve the flow and mechanics in RCB has been improved so as to make the solutions always converge even under high gas injecting pressures. A 2D hydro-chemical-mechanical problem is respectively solved by the original and the improved RCB code. The results are presented and compared.

***Keywords*—**CO2 storage, saline aquifer, RCB (RetrasoCodeBright), Geomechanics, Geochemistry.

I. 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 [1]. 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. Several CO2 storage projects are at present active, i.e. the SACS project (Saline Aquifer CO2 Storage) initiated 1998 in North Sea Utsira Formation reservoirs [2]; the CO_2SINK project started in April 2004 at Ketzin in Germany have demonstrated the big potential of saline aquifers for long term CO2 deposits [3]. More geologically CO2 sequestration projects are planned to start in the near future.

To study the migration, transformation and to predict the ultimate long term fate of CO_2 injected, reliable reactive flow modeling tools are needed. These reservoir models need to be capable of realistic modeling of the reaction rates for mineral dissolution as well as mineral precipitation. While several different codes are able to handle the flow of CO_2 in aquifers the number of codes for reactive flow simulators for this purpose is more limited. TOUGHREACT [4 -7] is one of the few examples. The ATHENA/ACCRETE simulator [8] is another example. Reservoir simulator ATHENA is built on the SOM (secondary oil migration) platform and developed into a platform for analyses of CO2 migration over long time scales and long distances.

While the sandstone in Utsira is geochemically simple in the sense that there is very limited amount of rapidly dissolving minerals, roughly 3% calcite, which dissolves on time scales of days at low pH. The rest of the Utsira lithology are minerals that dissolve at very long time scales. The geo-mechanical implication of mineral dissolution and precipitation in the Utsira formation is thus limited. Reservoirs with higher content of rapidly dissolving carbonates are among the worldwide interesting sites. Release of carbonate ions through dissolution in low pH zones will buffer the aqueous solution and contribute in keeping the pH on a higher level and thus slow down the further dissolution and corresponding mineral erosion. The question which remains is then for how long this buffering effect will last for realistic flow situation and the corresponding geo-mechanical implications of the erosion. Furthermore; transported ions may precipitate as minerals in regions of higher pH and thus change flow patterns and alter the local pressures. An additional effect is also the way the minerals are distributed and whether the dissolution of some minerals will lead to extensive release of remaining minerals as smaller particles which will be transported with the flow and may cause local reductions in permeability.

For some reservoirs it might also be desirable to locally fracture the reservoir in order to reduce the necessary inlet

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pressure for the CO2 injection. For this purpose it is also necessary to evaluate the geo-mechanical implications of the fracturing so as to evaluate that the formation as whole will still be geo-mechanically stable for the given injection scenario.

The geo-mechanical properties are implicitly coupled to the reservoir flow and it remains unverified whether or not explicit couplings between flow and geo-mechanics can mimic realistic CO2 storage scenarios.

In this work we describe an ongoing work in which we extend RetrasoCodeBright [9] into a high pressure simulator suitable for studies of CO2 storage scenarios. The original CodeBright [10 -13] contains an implicit algorithm for solution of the flow, heat-flow and geo-mechanical model equations. The Retraso extension of this code involves an explicit algorithm for updating the geochemistry, as schematically illustrated in fig. 1. Another advantage of this code, in addition to the implicit coupling between flow and geo-mechanics, is the large variety of advanced geo-mechanical models which can be applied in the analyses. This makes the code also suitable for studies of potential embrittlement of clay and shale due to reactions during long term contact with CO2.

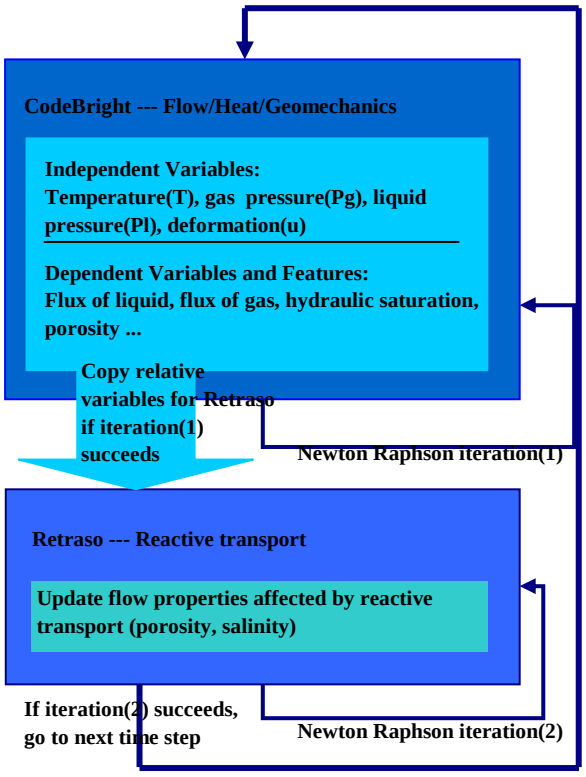


Fig 1 RCB solves the integrated equations sequentially in one time step.

The mathematical equations for the system are highly non-linear and are solved numerically [9]. The numerical approach can be viewed as divided into two parts: spatial and temporal discretization. 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 [10, 11].

RCB is a very advanced module for flow, heat, geomechanics and geochemistry calculation [12, 13]. Moreover, it has offered possibilities of just computing the chosen unknowns according to user if there are just a part of these unknowns are interested. For instance: hydro-mechanical, thermo-mechanical, hydro-thermal, hydro-chemical-mechanical, hydro-thermal-chemical-mechanical problems can be solved if the physical situation requires one of these approaches. Geometrically, RCB can handle problems in different dimensions, i.e. 1D, 2D and 3D [9 - 13].

The main limitations of the original RCB code, which limited its value for CO2 storage studies, are the assumption of ideal gas and divergence in the solution at pressures around 55 bars.

In this paper, RCB code is improved by doing three main corrections in implementation. The first two are the corrections for fugacity coefficients and Poynting corrections in the gas (CO2)/liquid equilibrium respectively in CodeBright part and Retraso part. These corrections are essentially straightforward to implement. The third correction is the density correction in the gas flow equations. These corrections also essentially straightforward give that the compressibility factors are known. Any equation of state can be used for this purpose provided that it adequately represents the fluids in consideration. The purpose of this paper is to describe the general features of the code and for this purpose we have used the SRK equation of state [14]. Other more accurate equations of state like for instance Span & Wagner [15] can be easily implemented since we use an interpolation scheme from a computed table in temperature, pressure, compressibility factor and fugacity. The extension to multi-component gas is also fairly straightforward.

The other optimization is done by modifying the conventional Newton-Raphson method, which introduces a relaxation factor α to make the iterative process converge faster. Nakata & Fujiwara [16] discuss various methods of searching for the relaxation factors. We develop the algorithm to get the proper relaxation factor in RCB code by combining the general tendency method [16] and time step reduction method. This method manages to make the iterative process converge regardless of the magnitude of the injection pressure.

In order to illustrate the impact of the non-ideal gas description we examine a simple constructed example in 2D. The results of some important hydraulic, mechanical and chemical features are put together in graphic window GiD [17].

II. MODIFICATIONS IN RCB CODE

A. Gas density correction

The gas phase in the original RCB is assumed to be at quite low pressures and behaves as ideal gas which obeys the ideal gas equation:

$$PV = nRT \quad (1)$$

This approximation will be failed in reality. We rewrite the gas equation as:

$$PV = ZnRT \quad (2)$$

where Z is the compressibility factor for the gas. Compressibility factor Z for CO2 is calculated using the SRK EOS tabulated as function of temperature T and pressure P and estimated by bilinear interpolation [8]. We can write the concentration of CO2 in gas phase (c_{co2}), expressed in mole per unit of volume, as:

$$c_{co2} = \frac{P}{ZRT} \quad (3)$$

And we can get the gas density of CO2 as:

$$\rho_{co2} = \frac{PM_{CO2}}{ZRT} \quad (4)$$

where P is pressures in bar, M_{CO2} is molar weight of CO2 (44.01 g/mol), R is the gas constant (8.3143 $J \cdot K^{-1} \cdot mol^{-1}$) and T is temperature in Kelvin.

Partial derivative of CO2 density with pressure at constant temperature is expressed as:

$$\left(\frac{\partial \rho_{CO2}}{\partial P}\right)_T = \frac{1}{Z \cdot RT} \cdot \left\{1 - P\left(\frac{\partial Z}{\partial P}\right)_T\right\} \quad (5)$$

where $\left(\frac{\partial Z}{\partial P}\right)_T = \frac{Z(T_x, P_2) - Z(T_x, P_1)}{P_2 - P_1}$, 1 or 2 is the subscripts address the table position in the Z *(T, P)* table.

B. Solubility of CO2

The bubblepoint mole fraction of CO2 is calculated according to:

$$x_{co2}^b = \frac{P\phi}{H_{co2}} \exp\left\{\frac{\overline{v}^{\infty}}{RT}(1-P)\right\} \quad (6)$$

where ϕ is the fugacity coefficient for CO2 estimated from the SRK equation of state, *H* is the

Henrys law coefficient for CO2, *P* is pressure (bar), *T* is temperature (K), *R* is the gas constant, and $\overline{v}^{\infty}$ is the partial molar volume of CO2 at infinite dilution. The fugacity coefficient is calculated as a function of temperature and pressure by a polynomial that is interpolated from SRK data. Similarly is the Henrys law coefficient found from a polynomial that is interpolated as a function of temperature and salinity from listed experimental data in [8]. The exponential term in equation (6) is the Poynting correction to the Henrys law coefficient.

C. Modifying Newton-Raphson scheme in CodeBright

When nonlinear hydro- mechanics system is analyzed by using the conventional Newton-Raphson method, the iterative process often fails to provide convergent solutions [18, 19]. It is the reason why when boundary CO2 injecting pressure is higher than 55 bars, iteration in the old RCB code can not manage to carry on.

The governing equations for non-isothermal multiphase flow of liquid and gas through porous deformable saline media have been established by Olivella et al. (1994). Variables and corresponding equations are tabulated as the following:

TABLE I
EQUATIONS AND VARIABLES

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

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

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

where **r** are the residuals, *d***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:

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

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:

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

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

If the optimum relaxation factor α_m [16], which minimizes the total square residual for the Galerkin method, is introduced at each step of the nonlinear iteration, convergent solution can be always obtained [16]. However, it takes very

long time to find to find α_m, because a large number of repeating calculations of square residual is required.

Here we define the objective function W [16] which is the total square residual of the Galerkin method as following:

$$W^{(k+1)} = \sum_{i=1}^{nu} \left\{ G_i^{(k+1)} \right\}^2 \qquad (10)$$

where nu is the number of unknown variables.

The relaxation factor is determined so that the objective functions $W^{(k+1)}$ at the (k+1)-th step of the nonlinear iteration is less than $W^{(k)}$ at the previous step as follows:

$$W^{(k+1)} < W^{(k)} \qquad (11)$$

The relaxation factor which satisfies (11) is searched for by using the following equation:

$$\alpha^{(k)} = 1/2^n \quad (n = 0,1,...,i) \qquad (12)$$

When (11) is satisfied, the calculation of (12) changing n is determined at $n = i$.

III. A 2D HYDRO-MECHANICAL-CHEMICAL EXAMPLE

This example illustrates a simple 2D saline aquifer with CO2 injection case.

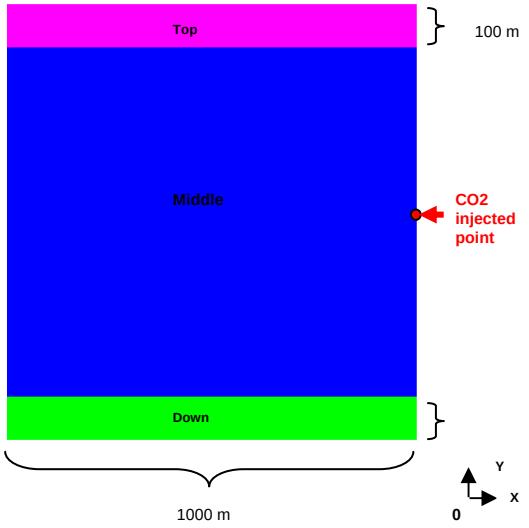


Fig.2 Geometry of the 2D reservoir and the CO2 injecting point

The geometry of this 2D domain is a 1000 m x 1000 m square. There are two different kinds of geological structures in the whole domain as illustrated with two different colors. The pink zone (Top) and green zone (Down) has the same geological structure. And the blue zone (Middle) has different geological structure. Each of "Top" and "Down" zones is a 1000m x 100m rectangular; while the blue zone is a 1000m x 800m rectangular. CO2 is injected into the middle point of the right boundary.

Initially, there is fine grained sand of pure calcite and its saturate solution in the "Middle" zone. In "Top" and "Down" zones, there are fine grained sand of 3% calcite and 97% quartz. The CO2 injecting pressure is 120 bars. Temperature does not change in the whole process. It is kept 25 Celsius in the whole area from the injection started.

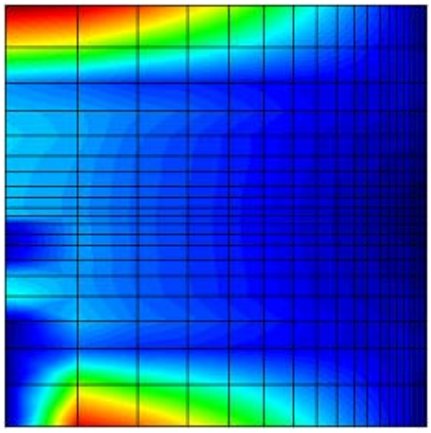
The initial liquid pressure and gas pressure in the 2D reservoir are respectively 50 bars and 30 bars. Except the boundary on the left side, neither liquid nor gas can infiltrate through other boundaries. Except the boundary on the right side, every boundary has displacements restriction. It is assumed that there are no initial displacements and no initial stress in the whole area.

IV. RESULTS AND DISCUSSIONS

The simulation results for hydraulic, mechanic movements and chemical transport in the 2D saline aquifer processed by improved RCB code can be visualized in GiD window [17]. Information about quite a few geomechanical and geochemical features can be got to know from this visual window. Here different evolution time points have been chosen at which some important features describing the changing in geometry, liquid and gas transport are illustrated for comparison for that CO2 is treated as ideal gas and a real fluid with gas density correction and CO2 solubility correction. They are liquid phase flux, pH value, porosity and stress.

Simulated results for the liquid flux 420 days after start of injection is plotted in fig.3. pH values after 13 days, 116 days and 420 days are plotted in figures 4, 5 and 6 respectively. Porosity and stress after 420 days are plotted in figures 7 and 8 respectively.

A. Liquid phase flux



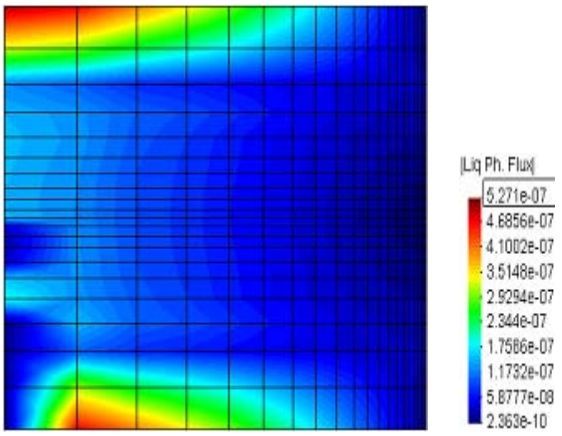


Fig.3 Plotted simulated results of liquid phase flux (m/s) at the time points of 420 days after CO2 injected as ideal gas (Top) and as real fluid (Bottom).

B. pH value

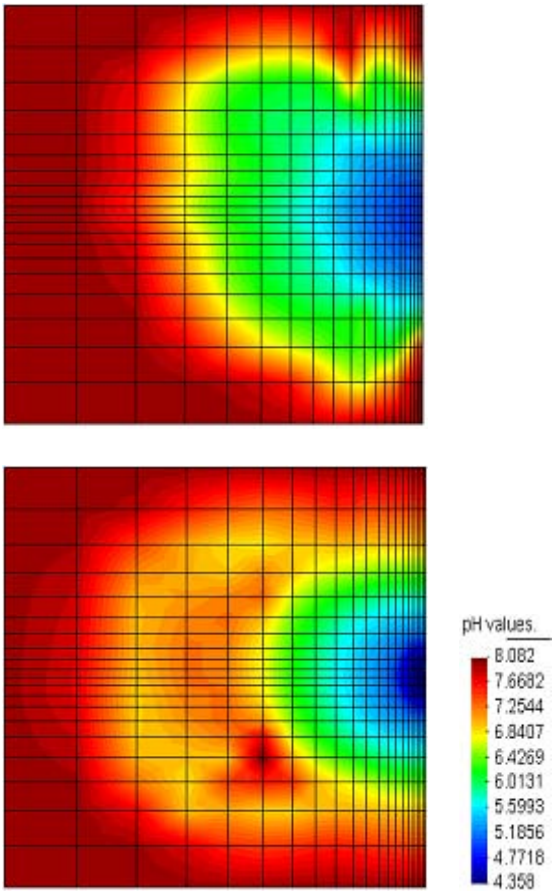


Fig.4 Plotted simulated results of pH values at the time points of 13 days after CO2 injected as ideal gas (Top) and as real fluid (Bottom).

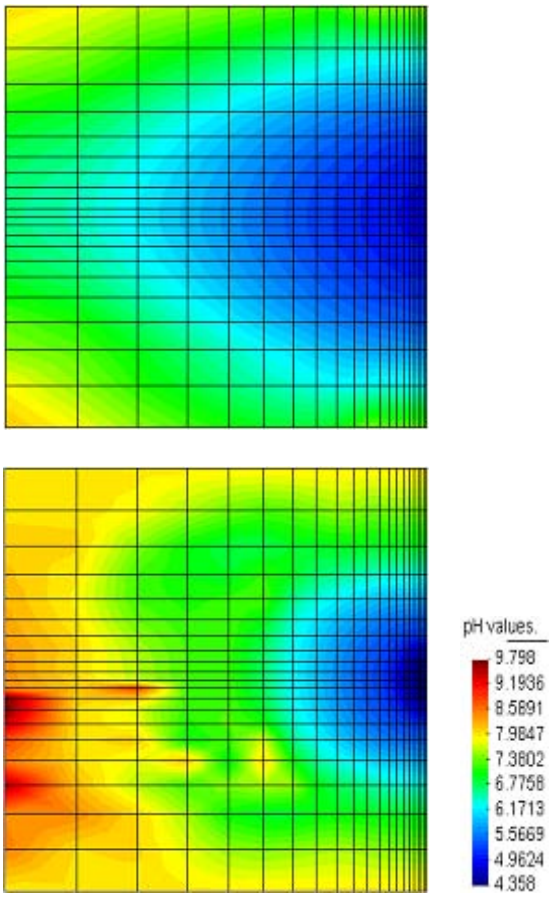


Fig.5 Plotted simulated results of pH values at the time points of 116 days after CO2 injected as ideal gas (Top) and as real fluid (Bottom).

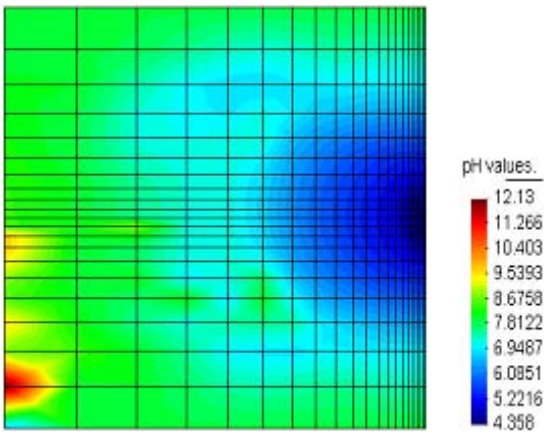


Fig.6 Plotted simulated results of pH values at the time points of 420 days after CO2 injected as ideal gas (Top) and as real fluid (Bottom).

C. Porosity

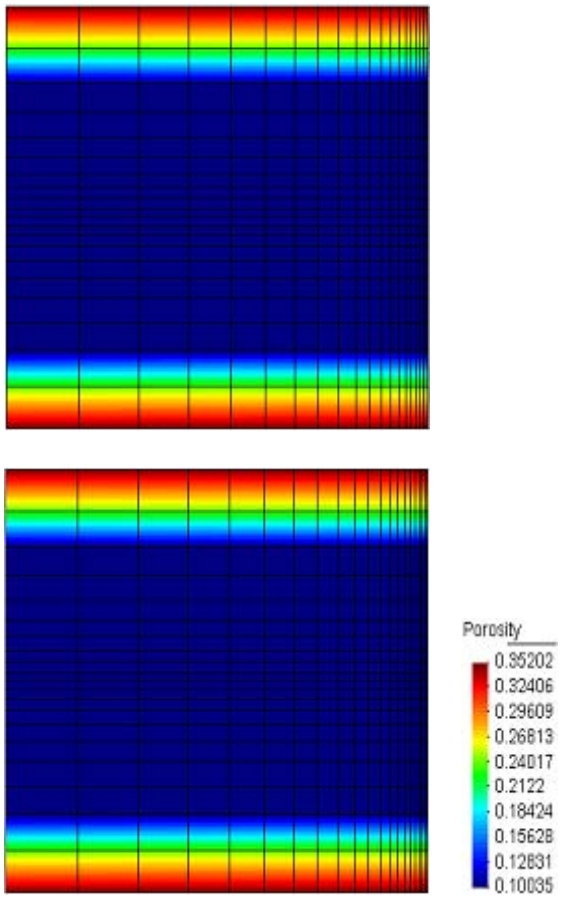


Fig.7 Plotted simulated results of porosity at the time points of 420 days after CO2 injected as ideal gas (Top) and as real fluid (Bottom).

D. Stress

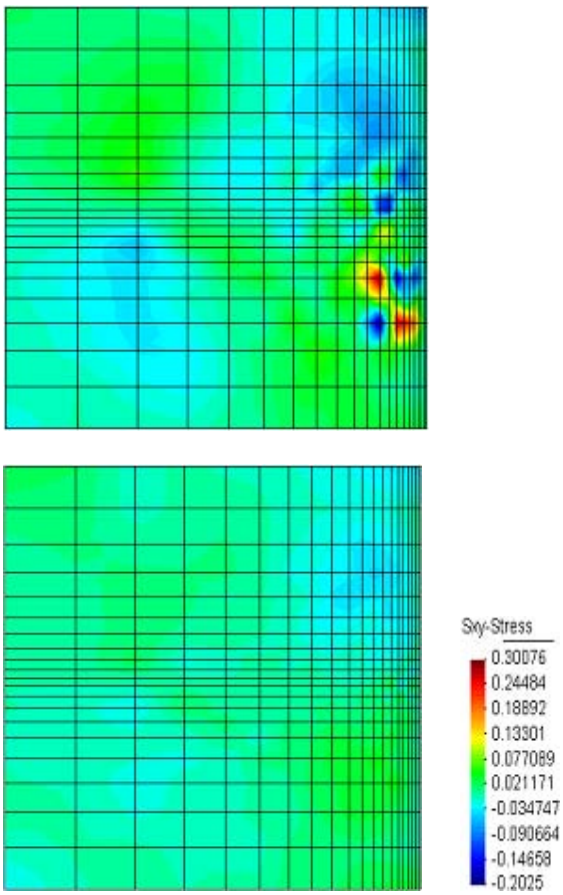


Fig.8 Plotted simulated results of stress at the time points of 420 days after CO2 injected as ideal gas (Top) and as real fluid (Bottom).

Results have proved that this modification is still effective when it is used in the complex flow-mechanic equations and chemical equations. Available injecting pressure limit for convergence is raised from 55 bars to significantly higher pressures. So far we have tested the code for the example system for pressures up to 140 bar. With adjusting the geo-mechanical and geochemical parameters code RCB can be implemented with good convergence.

The corrected version of the RCB code has been applied to a simple test case containing an inner section (80%) of pure calcite and two equal section of quartz (97%) and calcite.

Keeping in mind that the flow is driven by a constant difference in the injection pressure and the pressure on the left side of the model formation there are some properties which will not be very much affected by the transition from ideal gas to real gas description. Dissolution of calcite carbonate, the rapidly dissolving mineral, in the low pH regions leads to a buffering effect due to released carbonate ions that shifts the dissolution reactions towards less dissolved CO2. But the ions are transported with the reservoir fluid flow and the question is the balance between the buffering and the erosion due to dissolved carbonates and ion transport away from the vicinity of the injection region. The most pronounced effects are in the dissolved gas and corresponding pH, in which the buffering

effect is very clear. The increased buffering in the real gas case results in significantly higher pH values for the real gas case. But for both cases the pH remains above 5 in all regions and the corresponding effects on erosion is limited for ideal gas case as well as real gas case. Within the simulated period the effects on porosity and stress is very limited for this special example. But the ideal gas case exhibits some regions of relatively high stress close to the injection.

The contrast of dissolved CO2 gas in liquid between the situation of CO2 as ideal gas and CO2 as non-ideal fluid illustrates that ideal gas dissolves more easily due to the buffering effect.

The corrected version of the RCB code has been applied to a simple test case containing an inner section (80%) of pure calcite and two equal section of quartz (97%) and calcite. As expected the buffering effect is substantial during the maximum simulation time of 100 years. For this specific example the erosion and corresponding geomechanical instability effects are very limited for the actual injection rates.

V. Conclusions

We have extended a geomechanical reactive transport simulator RetrasoCodeBright into high pressures relevant for reservoir storage of CO2. Corrections for non-ideal gas has so far been based upon the SRK equation of state but can easily be replaced by similar results from any equation of state since the necessary data are interpolated from calculated tables of compressibility factors and fugacities as function of temperature and pressure. In addition the convergence of the Newton-Raphson iterative solution has been improved through implementation of an algorithm that minimizes the total square residual for the Galerkin method after each Newton-Raphson step. The corrected version has been applied to a simple test case with high buffering effect (a dominating section of pure calcite). For the particular test case the erosion is very limited and the corresponding geomechanical implications of the CO2 injection estimated to be correspondingly small, even for time periods up to 100 years.

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References

[1] Haszeldine, R. S., “Deep geological CO2 storage: principles reviewed, and prospecting for bioenergy disposal sites”, Proceedings from ACC Strategy, September 30 – October 1, 2004, Union Internationale des Chemins des Fer, Paris, http://www.accstrategy.org/simiti/Haszeldine.pdf

[2] Hellevang, H., Khattri, S.K., Fladmark, G. E., Kvamme, B. CO2 storage in the Utsira Formation: ATHENA 3-D reactive transport simulations, 2007, Submitted to the journal of Basin Research

[3] CO2SINK, a research project of CO2 storage in underground geological formation in Ketzin, Germany, http://www.co2sink.org/

[4] Pruess, K. and J. García. Multiphase Flow Dynamics During CO2 Injection into Saline Aquifers, *Environmental Geology*, Vol. 42, pp. 282 - 295, 2002

[5] Dobson, P. F., Kneafsey, T. J., Sonnenthal, E. L., Spycher, N., and Apps, J. A., Experimental and numerical simulation of dissolution and precipitation: implications for fracture sealing at Yucca Mountain, Nevada, *Journal of Contaminant Hydrology*, v. 62-63, p. 459-476, 2003.

[6] Dobson, P. F., Salah, S., Spycher, N., and Sonnenthal, E. L., Simulation of water-rock interaction in the Yellowstone geothermal system using TOUGHREACT, *Geothermics*, v. 33, p. 493-502, 2004. Kim, J., Schwartz, F. W., Xu, T., Choi, H., and Kim, I. S., Coupled processes of fluid flow, solute transport, and geochemical reactions in reactive barriers, *Vadose Zone Journal*, v. 3, p. 867-874, 2004.

[7] Kiryukhin, A., T. Xu, K. Pruess, J. Apps, and I. Slovtsov, Thermal-hydrodynamic-chemical (THC) modeling based on geothermal field data, Geothermics, 33(3), 349-381, 2004.

[8] Hellevang, H., Kvamme, B, “*An explicit and efficient algorithm to solve kinetically constrained CO_2-water-rock interactions*”, 2007, WSEAS TRANSACTIONS on Mathematics, 6, issue 5, 681 – 687, ISSN: 1109-2769

[9] Saaltink, M., Benet, I., Ayora, C., RETRASO, Fortran Code for Solving 2D Reactive Transport of Solutes, Users´s guide. Barcelona, E.T.S.I. Caminos, Canales y Puertos, Universitat Politecnica de Catalunya and Instituto de Ciencias de la Tierra, CSIC, 90 pp. 1997

[10] Saaltink, M., Batlle, M., Ayora, C., “RETRASO, a code for modeling reactive transport in saturated and unsaturated porous media”, Geologica Acta, Vol.2, No 3, pp. 235-251, 2004

[11] Olivella, S., A. Gens, J. Carrera, E. E. Alonso, “Numerical Formulation for a Simulator (CODE_BRIGHT) for the Coupled Análisis of Saline Media”, Engineering Computations, vol. 13, No.7, pp.87-112, 1996

[12] Olivella, S., A. Gens, J. Carrera, CodeBright User’s Guide. Barcelona, E.T.S.I. Caminos, Canales y Puertos, Universitat Politecnica de Catalunya and Instituto de Ciencias de la Tierra, CSIS, 1997

[13] Olivella, S., J. Carrera, A. Gens, E.E. Alonso, “Non-isothermal Multiphase Flow of Brine and Gas through Saline Media”, Transport in Porous Media, 15, pp. 271-293, 1994

[14] Soave, G., “Equilibrium constants from a modified Redlich-Kwong equation of state” Chem. Eng. Sci., 27,1197-1203, 1972.

[15] Span, R. and W. Wagner. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa, *J. Phys. Chem. Ref. Data*, Vol. 25, No. 6, pp. 1509 - 1596, 1996

[16] Nakata, T. and Fujiwara, K., “Method for determining relaxation factor for modified Newton-Raphson method”, IEEE TRANSACTIONS ON MAGNETICS, vol. 29, No. 2, MARCH 1993

[17] CIMNE, International Center For Numerical Methods and Engineering, “GiD – The personal pre- and post processor”, http://gid.cimne.upc.es/

[18] Nakata, T, Takahashi, N., Fujiwara, K., Okamoto, N. and Muramatsu, K. "Improvements of convergence characteristics of Newton-Raphson method for nonlinear magnetic field analysis," IEEE Trans Magn., vol. M 28, no.2, pp. 1048-1051, March 1992.

[19] Nakata, T, Takahashi, N., Fujiwara, K., Olszewski, P., and Muramatsu, K. "Analysis of magnetic fields of 3-D non-linear magnetostatic model (Problem 13)," Proceedings of the European TEAM Workshop and International Seminar on Electromagnetic Field Analysis, pp. 107-1 16, 1990.