

SIMULATION OF HYDRATE DYNAMICS IN RESERVOIRS

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ABSTRACT

Gas hydrates in reservoirs are generally not in thermodynamic equilibrium and there may be several competing phase transitions involving hydrate. Formation of carbon dioxide hydrates during aquifer storage of carbon dioxide involves roughly 10% volume increase compared to groundwater. Dissociation of hydrate towards under saturated fluid phases involves the same level of contraction. Hydrate phase transitions are generally fast (scales of seconds) compared to mineral dissolution and precipitation and it is unlikely that a time shifted explicit coupling to geo mechanical analysis will be able to capture the appropriate dynamic couplings between flow and changes in stress. The need for geo mechanical integrity of the storage site therefore requires a reservoir simulator with an implicit solution of mass flow, heat flow and geo mechanics. And since carbon dioxide involved in hydrate is also involved in different geochemical reactions we propose a scheme where all possible hydrate formation (on water/carbon dioxide interface, from water solution and from carbon dioxide adsorbed on mineral surfaces) as well as all different possible dissociations are treated as pseudo reactions but with kinetics derived from advanced theoretical modelling. The main tools for generating these models have been phase field theory simulations, with thermodynamic properties derived from molecular modelling. The detailed results from these types of simulations provides information on the relative impact of mass transport, heat transport and thermodynamics of the phase transition which enable qualified simplifications for implementation into RCB. The primary step was to study the effect of hydrate growth or dissociation with a certain kinetic rate on the mechanical properties of the reservoir. Details of the simulator, and numerical algorithms, are discussed in detail and some relevant examples are shown.

Keywords: gas hydrates, CO₂ storage, RCB, hydrate formation.

INTRODUCTION

Background

Carbon dioxide is an important green house gas and one of the promising options to reduce the emissions of CO₂ is storage of CO₂ in deep saline aquifers [1]. Saline aquifers are water bearing porous layers of permeable rocks like sandstone or limestone; they are widespread and have high potential for the large scale storage of CO₂ gas. A variety of industrial processes emit large amounts of CO₂, for example oil refineries, cement works,

and iron and steel production, thermal power plants. These emissions could be reduced substantially, without major changes to the basic process, by capturing and storing the CO₂. Some examples of CO₂ storage projects in saline aquifers sites are Saline Aquifer CO₂ Storage (SACS) at Sleipner, which was the first industrial scale project. A Million ton of CO₂ per year is separated from the natural gas produced from the Sleipner field using amine solvents and then injected into the Utsira formation in supercritical

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state. Injection has been going on since 1996[2, 3]. Second project on Norwegian margins is storage of CO₂ from the Snøhvit gas field, which started in April 2008. This field is located in the Barents Sea and 700,000 tonnes per year is stored deep down under the hydrocarbon bearing formation [4]. European research project (CO₂SINK) in Ketzin, Germany started in April 2004 and CO₂ injection started from June 2008[5]. In Salah, an industrial-scale Carbon Capture and Storage (CCS) project in Algeria has been in operation since 2004. More than three million tonnes of CO₂ separated during gas production have been securely stored in a deep saline formation. BP, Sonatrach and Statoil, the project operators, aim to store a total of 17 million tonnes over the next 20 years [6]. In Italy a CCS demonstration facility at Porto Tolle intend to capture CO₂ present in the flue stream from a power plant, then compressing, transporting and storing it in a saline aquifer. Underground storage is planned to start by 2015[7]. In Belchatów, Poland, lignite-fired energy plant is developing a demonstration scale CCS installation integrated with the newly-built 858 MW unit since 2007 which is planned to start from 2013[7]. With these examples, and numerous other planned CO₂ storage projects worldwide, theoretical evaluation of storage integrity is an important task since monitoring only can capture the short time scales and long term storage safety is an important issue for governmental institutions approving the different projects as well as for the public perception.

RetrasoCodeBright

In studies of CO₂ migration during storage of CO₂ in aquifers or depleted hydrocarbon reservoirs the possibility of CO₂ hydrate formation have to be evaluated and corresponding geo-mechanical impact have to be analysed. For reservoirs where hydrate may form in some regions hydrate formation involves roughly 10% volume increase of water. In parallel to this there are chemical reactions which can supply extra CO₂ though dissolution of carbonates in regions of low pH, and also region of high pH where transported ions may precipitate and even extract CO₂ from water and hydrate. The formed hydrate will not be in equilibrium (Gibbs phase rule). Neither will it attach to the mineral surfaces due to incompatibilities of hydrogen bonds in hydrate and interactions with atomic partial charges on the mineral surfaces. For this reason there is a need for

a logistic system that can handle competing processes of formation and dissociation. A reactive transport simulator can handle that. Implicit geo mechanics is needed in order to handle competing phase transitions which are very rapid (seconds) and dynamically coupled to geochemical reactions which can be fairly fast (hours to days). For this purpose a reactive transport reservoir simulator, Retraso CodeBright(RCB), is used in this study and extended with hydrate phase transitions as "pseudo reactions". RCB is capable of realistic modelling of the reaction rates for mineral dissolution and precipitation, at least to the level of available experimental kinetic data. In contrast to some oil and gas simulators the simulator have flow description ranging from diffusion to advection and dispersion [8, 9] and as such is able to handle flow in all regions of the reservoir, including the low permeability regimes of hydrate filled regions. In contrast to the Utsira injection from Sleipner, which is outside hydrate stability zones, there are regions of hydrate stability in the Snøhvit storage case [3, 4]. If a CO₂ plume enters these regions there is a need for knowledge on the impact of hydrate formation on reduced permeability and flow implications and also on the possible impact of hydrate formation on geo-mechanics.

The mathematical equations for the system are highly non-linear and 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 Newton-Raphson method is adopted for the iterative scheme[8, 9].

A brief overview of independent variables, constitutive equations and equilibrium restriction are given in Table 1 and Table 2 respectively.

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 in Table 1.

Constitutive equations and equilibrium restrictions

Associated with this formulation there is a set of necessary constitutive and equilibrium laws. Table 2 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.

Equation	Variable Name
Equilibrium of stresses	Displacements
Balance of liquid mass	Liquid pressure
Balance of gas mass	Gas pressure
Balance of internal energy	Temperature

Table 1 Equations and independent variables

Constitutive Equation	Variable Name
Darcy's Law	Liquid and gas advective flux
Fick's law	Vapour and gas non-advective flux
Fourier's law	Conductive heat flux
Retention curve	Liquid phase degree of saturation
Mechanical constitutive model	Stress tensor
Phase density	Liquid density
Gas Law	Gas density
<i>Equilibrium restrictions</i>	<i>Variable name</i>
Henry's law	Air dissolved mass fraction
Psychometric law	Vapour mass fraction

Table 2 Constitutive equations and equilibrium restrictions

RCB is a coupling of a reactive transport code Retraso with a multiphase flow and heat code CodeBright. CodeBright contain an implicit algorithm for solution of flow, heat-flow and geo-mechanical model equations [10-12]. The Retraso extension of CodeBright involves an explicit algorithm for updating the geochemistry [8, 9] as shown in the Figure 1. This new coupled tool RCB is capable of handling both saturated and unsaturated flow, heat transport and reactive transport in both liquid and gas. It is a user friendly code for flow, heat, geo-mechanics and geochemistry calculation. It offers possibility to just computing the chosen unknowns of user's interest such as hydro-mechanical, hydro-chemical-mechanical, hydro-thermal, hydro-

thermal-chemical-mechanical, thermo-mechanical etc.

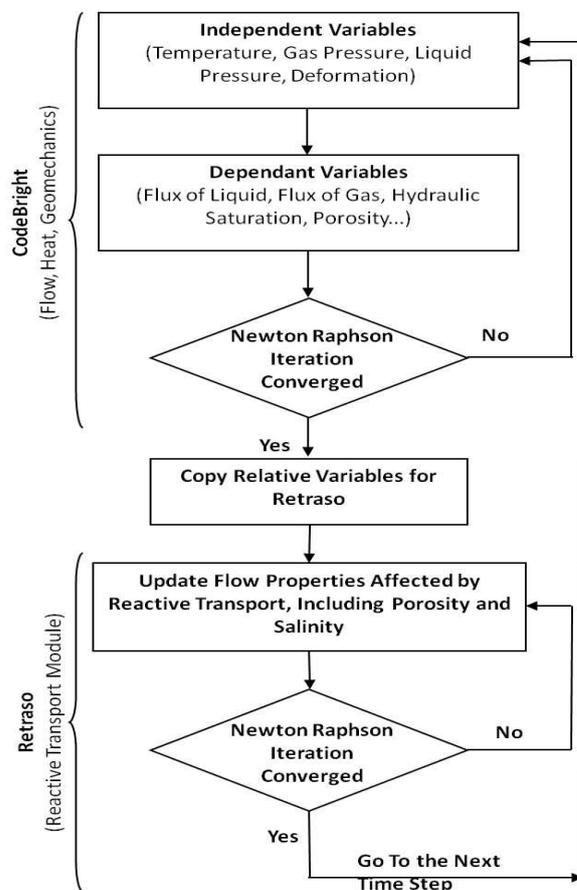


Figure 1 RCB solves the integrated equations sequentially in one time step

It can handle problems in 1D, 2D and 3D dimensions [8-12]. An important advantage of RCB is the implicit evaluation of geo-mechanical dynamics. According to the Figure 1, flow, heat and geo-mechanics are solved initially in CodeBright module through Newton-Raphson iteration and then the flow properties are updated according to the effects of reactive transport on porosity and salinity in a separate Newton Raphson procedure but for the same time step [8, 9]. This makes it possible to study the implications of fast kinetic reactions such as hydrate formation or dissociation more realistically. Hydrate in the reservoir can form from different phases such as liquid phase, gas phase and adsorbed phase on minerals and according to the phase rule there will be always several competing reactions that will prevent the system from reaching equilibrium. For

instance hydrate formation rate from $\text{CO}_2(\text{g})+\text{H}_2\text{O}(\text{l})$ will not be the same as $\text{CO}_2(\text{aq})+\text{H}_2\text{O}(\text{l})$. Because of this non-equilibrium nature of hydrate in the reservoir, it is very important to consider the kinetics of hydrate formation and dissociation for all possible scenarios [13]. For this purpose, non-equilibrium thermodynamics of hydrate should be employed to determine the kinetic rates of different competing scenarios in each node and each time step according to the temperature, pressure and composition of the system. In this study CO_2 hydrate is added into the simulator as a pseudo-mineral component with a constant kinetic rate for hydrate formation and dissociation so that hydrate formation possibility can be studied when CO_2 migrates upwards in the aquifer. Hydrate formation and dissociation can directly be observed through porosity changes in the specific areas of aquifer. Porosity reduction indicates hydrate formation and porosity increase indicates hydrate dissociation. Temperature, pressure and CO_2 concentration in all possible phases are three factors, which influence hydrate formation or dissociation. The kinetic rate used in this study is calculated from extrapolated results of phase field theory simulations by Svandal et al. [14]. In the next stage, it will be replaced by a thermodynamic code, which is already in the final stages, to account for all different competing reactions. This feature of non-equilibrium evaluation of hydrate distinguishes RCB from all other academic and commercial hydrate simulators available today. To illustrate impact of hydrate formation on the reservoir geo-mechanical properties a simple 2D model case was constructed. The results from this model for some important mechanical, hydraulic properties were assembled and illustrated through a graphical window GiD [15].

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 complexation (including redox reactions) and adsorption. The density of CO_2 plumes which accumulate 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 of clay. Mineral reactions between CO_2 and shale minerals are additional effects which eventually may lead to embrittlement. Linear geo-mechanics may not be appropriate for these effects. Clay is expected to exhibit elastic non-linear contributions to the geo-mechanical properties. Different types of nonlinear 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/or experiments. The current version of RCB has been extended from ideal gas into handling of CO_2 according to the SRK equation of state [16]. This equation of state is used for density calculations as well as the necessary calculations of fugacities of the CO_2 phase as needed in the calculation of dissolution of CO_2 into the groundwater [17]. The dissolution and precipitation of minerals in CO_2 injection scenarios are, with the exception of some carbonates, slow natural processes and in our example mineral/fluid reactions are described by built-in kinetics based on available experimental data from open literature [18]. The mathematical equations for the system are highly non-linear and solved numerically [8, 9].

Two Dimensional Model's Description

The geometry of the 2D domain is 1000 m x 250 m rectangle. There are 2 aquifers, 2 caprocks and 1 fracture zone in this geometry. Bottom Aquifer is a 1000 m x 150 m rectangle and top aquifer is 1000 m x 50 m rectangle. Caprocks are in between top and bottom aquifers and very thin fracture zone exists in the middle of two caprocks as shown in the Figure 2. Caprocks are 498 m x 50 m rectangles each and fracture is very thin rectangular of dimension 4 m x 50 m. CO_2 is injected at the right-down corner in the bottom aquifer. Compositions of rocks in each zone are as follows; both aquifers have porosity 0.1 and among minerals they have 3.6% calcite, 86.4% quartz. Caprocks have similar composition and porosity, porosity for both of them is 0.01 and there is 4% calcite and 95% quartz present. For fracture, porosity is 0.05 and 3.8% calcite and 91.2% quartz is present in it. Pressure and temperature at each node are defined in one of the input files. In the reservoir pressure gradient is 1.0 MPa/100m and temperature gradient is 3.6 °C/100m. CO_2 Injection pressure is 5.1 MPa. Pressures boundaries are also defined at top and bottom of the reservoir, at top 2.5 MPa and at

bottom 5 MPa pressure boundaries enclose the reservoir.

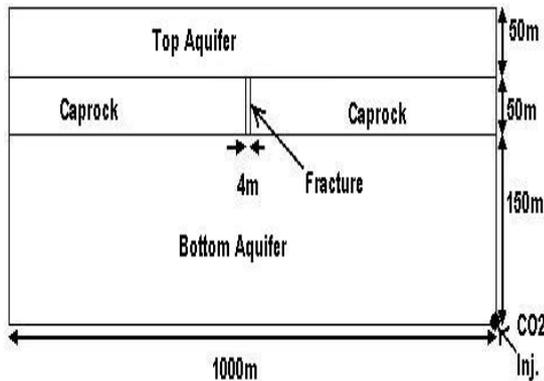


Figure 2 Geometry of 2D model with CO2 Injection point

Species	Aquifers	Caprocks	Fracture
Aqueous	ca+2 , h2o , hco3- , oh- , sio2(aq)	ca+2 , h2o , hco3- , oh- , sio2(aq)	ca+2 , h2o , hco3- , oh- , sio2(aq)
Mineral Volume Fraction	calcite (.036) quartz (.864)	calcite (.04) quartz (.95)	calcite (.038) quartz (.912)
Gas	CO2	CO2	CO2

Table 3 Chemical Species in different forms

Parameter	Bottom Aquifer	Top Aquifer	Cap rocks	Fracture
Pressure, (MPa)	3.5-5	2.5-3	3-3.5	3-3.5
Temperature, (°C)	8.6-14	5-6.8	6.8-8.6	6.8-8.6
Mean Stress (MPa)	7.87-10.97	5.65-6.76	6.76-7.87	6.76-7.87
CO2 Injection Pressure (MPa)	4.6	-	-	-
Gas and Liquid outgoing Pressure (MPa)	-	2.5	-	-

Table 4 Initial and Boundary Conditions, values vary with depth so they are in range

Property	Aquifers	Caprocks	Fracture
Young's Modulus (GPa)	0.3	0.3	0.3
Poisson's Ratio	0.2	0.2	0.2
Zero stress porosity	0.1	0.01	0.05
Zero stress permeability, (m ²)	1.0e-13	1.0e-17	1.0e-12
Van Genuchten's gas entry Pressure, (kPa), (at zero stress)	196	196	196
Van Genuchten's exponent, m	0.457	0.457	0.457
Thermal Conductivity of Dry Medium (W/m K)	4.64	4.64	4.64
Thermal Conductivity of Saturated Medium (W/m K)	2.64	2.64	2.64

Table 5 Material Properties

Table 3, 4 and 5 contain data related to chemical species, initial pressure and temperature ranges for reservoir nodes, boundary condition and material properties.

RESULTS AND DISCUSSION

The simulation results processed by RCB are visualized using GiD visual window [15]. Porosity, gas phase flux, liquid phase flux, heat flux, liquid saturation, temperature, stress, gas and liquid pressures are among the properties which can be visualised in GiD platform presently and only limited to what is printed out from RCB in formats that GiD can read. Porosity, gas phase flux, gas pressure and development of stress are plotted as illustrations of the changes during hydrate formation. This is a simple test case and as such no geomechanical analysis is conducted here but it will be available through the average

calculated pore pressure and the stresses in figure 5 below.

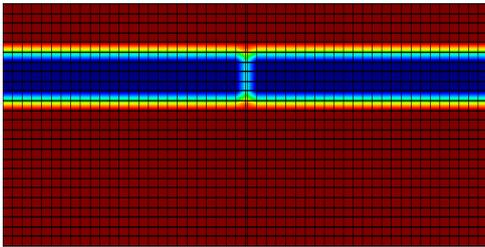


Figure 3a Porosity after 7 days

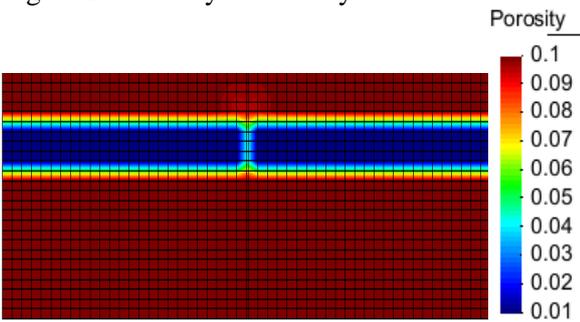


Figure 3b Porosity after 235 days

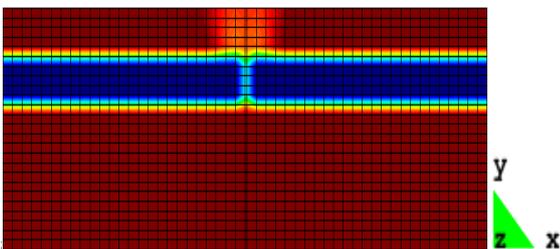


Figure 3c Porosity after 257 days

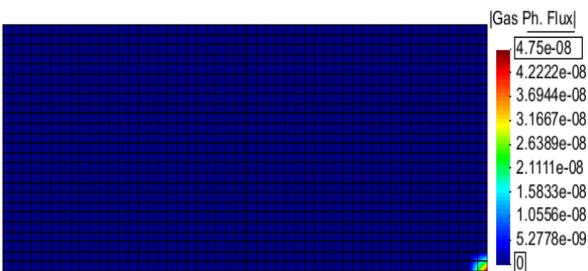


Figure 4a Gas Phase Flux(m/s) after 7 days

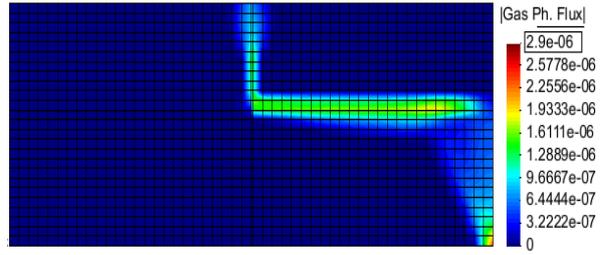


Figure 4b Gas Phase Flux(m/s) after 235 days

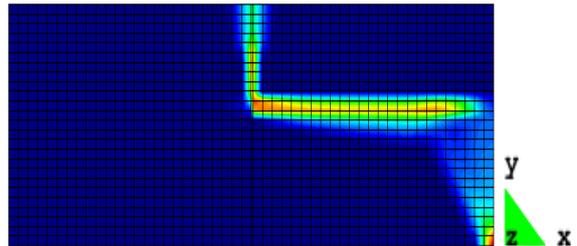


Figure 4c Gas Phase Flux(m/s) after 257 days

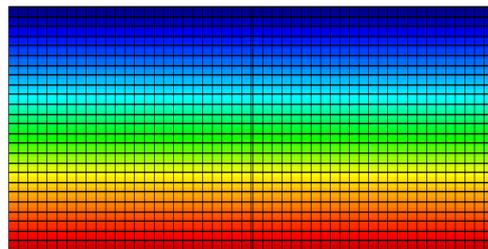


Figure 5a Gas Pressure(MPa) after 7 days

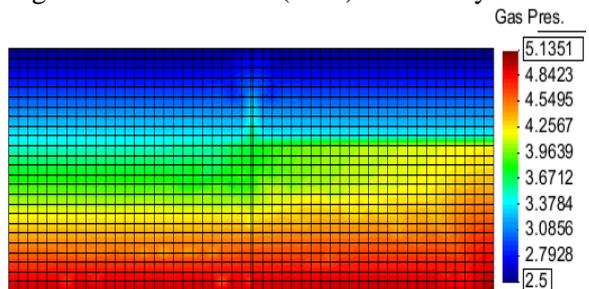


Figure 5b Gas Pressure(MPa) after 235 days

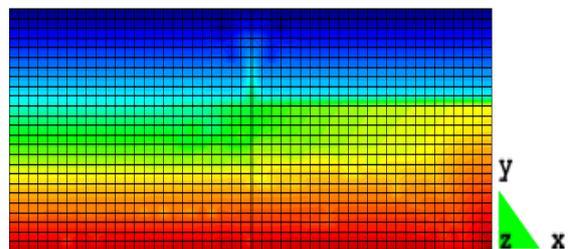


Figure 5c Gas Pressure(MPa) after 257 days

Simulation results for mean stresses after 257 days is shown in Figure 6, initial mean stresses are tabulated in Table 3.

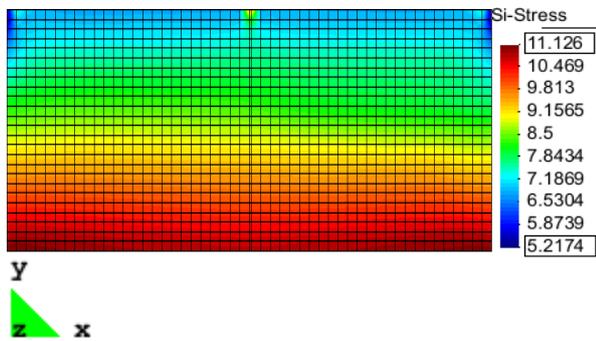


Figure 6 Mean Stress(MPa) after 257 days

Development of porosity (see fig. 3), and consequences for development of gas flux (fig. 4) due to hydrate formation, i.e. pseudo mineral precipitation, as function of time over different regions of the reservoir gives indication on negative and positive sides of the hydrate formation. Reduction in porosity results in altered permeability and quickly affects the spreading of CO₂ in the horizontal direction, as can be seen from figure 4 for this specific example case. Calculated results for gas pressure are plotted in Figures 5a,5b,5c after same times as porosity and gas flux; 7, 235 and 257 days respectively. Gas phase flux units range for Figure 4b and 4c is same.

From Figure 4b and 4c it is observed that CO₂ flux escaping through fracture zone has increased, which is logical for this pressure driven injection rate. It can be concluded that from the time of first outbreak, CO₂ flux through fracture increases with time, resulting in more CO₂ availability for hydrate reaction. It support hydrate formation "reaction" and porosity reduces faster afterward, this change is visible in Figure 3c. Figure 5a, 5b and 5c shows relative change in gas pressures in the reservoir with time. This illustrates the slow spreading of gas pressure in the horizontal direction due to reduced flow in the hydrate zones.

At this stage the implications of reduced porosity and changed saturations have been corrected for using the traditional correlations due to van Genuchten [19]. This needs of course to be corrected in future work since hydrate have completely different characteristics than minerals. And hydrate cannot even attach to the mineral surfaces as mention earlier. The closest distance to minerals surfaces will be roughly 2 - 3 nm based

on bridging though hydrate fluid interfaces and mineral fluid interfaces.

CONCLUSION

In this work we have demonstrated the implementation of CO₂ hydrate in RetrasoCodeBright and used a simple example to illustrate the impact of hydrate formation on reduced porosity, changed permeability and the overall impact of changed flow on stress development in different regions of the reservoir. This is the first step in further extensions to include competing phase transition of hydrate growth as well as dissociation toward under saturated phases. These hydrate phase transitions are in non-equilibrium and hydrates formed from different phases will generally have different compositions and different free energies. By treating the different hydrates as pseudo minerals the logistics of the reactive transport simulator and kinetic rates for the different formation situations from published results this represents a new framework for evaluation of aquifer storage in regions where hydrate formation may have an impact on storage integrity. Even if hydrates will not be able to block the sediments any reduction in vertical flow rates gives more time for CO₂ dissolution and corresponding sinking of CO₂ enriched groundwater. On the other hand, formation of CO₂ hydrate will reduce fluxes in the horizontal directions and as such have negative impact for the horizontal spreading of plumes unless this spreading is shifted to lower section of the reservoir where hydrate is not stable. Results from application of the simulator on a simple example with a top zone in hydrate forming conditions followed by a cap rock with a fracture and a sand layer show clearly that hydrate formation take places as soon as CO₂ breaks through fracture zone. Reduction in porosity indicates that solid hydrate is forming according to added hydrate formation reaction rate and the supply of CO₂ through the calculated flow.

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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, Union Internationale des Chemins des Fer, Paris, France 2004
- [2] Hellevang, H., Khattri, S.K., Fladmark, G. E., Kvamme, B. *CO₂ storage in the Utsira Formation: ATHENA 3-D reactive transport simulations*, Submitted to Journal of Basin Research, 2007
- [3] Erik Gøsta Bruno Lindeberg, chief scientist, SINTEF Petroleum and Energy, Trondheim. *Saline Aquifer CO₂ storage (SACS) project, Sleipner, Norway*. See Also: <http://www.sintef.net/Projectweb/IK-23430000-SACS/>
- [4] Statoil, *Carbon capture and storage project, Snøhvit, Norway*. Originally published 23-04-2008, Updated 29-10-2009. See also: <http://www.statoil.com/en/NewsAndMedia/News/2008/Pages/CarbonStorageStartedOnSnøhvit.aspx>
- [5] Dr. Hilke Wuerdemann, CO₂SINK Project Office, GFZ Potsdam, Germany, *CO₂SINK, a research project of CO₂ storage in underground geological formation in Ketzin, Germany*, See also: <http://www.co2sink.org/>
- [6] Allan Mathieson*, John Midgely, Iain Wright, Nabil Saoula, Philip Ringrose, *In Salah CO₂ Storage JIP: CO₂ sequestration monitoring and verification technologies applied at Krechba, Algeria* In: Proceedings of the Greenhouse Gas Control Technologies (GHGT) conference, Washington DC, USA, 2008.
- [7] Mrs C. La Marca, cristiana.lamarca@enel.com Deputy coordinator/Research Manager, Enel, Porto Tolle, Italy and Ms Dominika Kukiela, Dominika.kukiela@elb.pl, Belchatów, Poland Carbon capture and storage Projects, see also: <http://microsites.ccsnetwork.eu/porto-tolle>, <http://microsites.ccsnetwork.eu/belchatow>
- [8] 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
- [9] 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
- [10] Olivella, S., A. Gens, J. Carrera, E. E. Alonso, *Numerical Formulation for a Simulator (CODE_BRIGHT) for the Coupled Analysis of SalineMedia*, Engineering Computations, vol. 13, No.7, pp.87-112, 1996
- [11] 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
- [12] 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
- [13] Kvamme B., *Kinetics of Hydrate Formation from Nucleation Theory*, International Journal of Offshore and Polar Engineering Vol. 12, No. 4, December 2002 (ISSN 1053-5381)
- [14] Atle Svandal, *Modeling hydrate phase transitions using mean-field approaches*, PhD Thesis submitted to University of Bergen, February 2006
- [15] CIMNE, *International Center For Numerical Methods in Engineering*, gid@cimne.upc.edu, Barcelona, Spain. “GiD – The personal pre- and post processor”, See also: <http://gid.cimne.upc.es/>
- [16] Bjørn Kvamme*, Shunping Liu. *Reactive Transport of CO₂ in Saline Aquifers with implicit geomechanical analysis*. In: Proceedings of the Greenhouse Gas Control Technologies (GHGT) conference, Washington DC, USA, 2008.
- [17] Hellevang, H., Kvamme, B. *An explicit and efficient algorithm to solve kinetically constrained CO₂-water-rock interactions*, Proceedings of the 3rd WSEAS International Conference on Mathematical Biology and Ecology, Gold Coast, Queensland, Australia, January 17-19, 2007
- [18] Lasaga A.C., *Chemical kinetics of water-rock interactions*, Journal of Geophysical Research, B6, 4009-4025
- [19] van Genuchten, M.Th. *A Closed-Form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils*, Soil Sci. Soc. Am. J., Vol. 44, pp. 892 - 898, 1980.