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ACCRETE – Geochemistry solver for CO₂-water-rock interactions

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Abstract

Increasing atmospheric concentrations of greenhouse gases are suspected of causing a gradual warming of the Earth's surface. Because CO₂ is a significant greenhouse gas, storage in saline aquifers has been suggested as one possible approach to reduce emissions of CO₂. As a part of the “Long-term storage of CO₂ in saline aquifers” project at University of Bergen, a new geochemistry code ACCRETE has been developed to solve CO₂-water-rock interactions. This paper reports ACCRETE solutions to some of the key geochemical features of CO₂ storage, i.e. solubility of CO₂ in saline solutions, aqueous carbon speciation, pH, and kinetically constrained mineral reactions.

Keywords: CO₂, simulation, phreeqc, comparison, carbonate

Introduction

The three major storage mechanisms for CO₂ in aquifers are: (1) Trapping beneath low- or impermeable structures; (2) solubility trapping in aqueous solutions; and (3) permanent storage in solid carbonates. The first and second mechanisms are believed to be of major importance for the short-term (a few years) safety of injected CO₂, whereas the third mechanism may play a major role on longer timescales. The two former mechanisms are closely related to the rate of CO₂ consumption into the aqueous phase, which is a function of temperature, pressure, and salinity. This paper reports solubility data of CO₂ as a function of temperature, pressure and salinity for ACCRETE simulations, compared to data by Duan and Sun [1] and PHREEQC computations using data from thermo.com.V8.R6.230 [2]. The slow conversion of CO₂ to solid carbonates is strongly a function of the compositions of the aqueous phase and hence pH. Since the carbonate mineral reactions are expressed as a function of bicarbonate activity, the aqueous carbonate speciation is fundamental in understanding the reactivity of the solid carbon phases. Activities of the aqueous carbon species and pH as a function of partial pressure of CO₂ are presented here and compared to values estimated by PHREEQC. The last part of the paper focuses on the capability of ACCRETE to work as a geochemistry module in comprehensive reactive transport simulations.

Methodology and theoretical considerations

Thermodynamic database

Thermodynamic data is calculated with the SUPCRT92 code [3] using the dprons96.dat database. The standard state is that of unit activity for pure minerals and H₂O at any temperature and pressure. For aqueous species other than H₂O, the standard state is unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any

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temperature and pressure. For gases, the standard state is for unit fugacity of a hypothetical ideal gas at 1 bar pressure.

Solubility of CO₂

The bubblepoint mole fraction of CO₂ is calculated according to:

$$x_{CO_2}^b = \frac{P\phi}{H_{CO_2}} \exp\left\{\frac{\bar{v}^\infty}{RT}(1-P)\right\}, \quad (1)$$

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 \bar{v}^∞ 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 [4]. The exponential term in equation (1) is the poynting correction to the Henrys law coefficient.

Table 1 Equilibrium reactions included in the ACCRETE code.

Equilibrium reactions	$\log_{10}(K)$
$H_2O + CO_{2,aq} \leftrightarrow HCO_3^- + H^+$	-6.345
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	-10.329
$H_2O \leftrightarrow H^+ + OH^-$	-13.995
$Na^+ + HCO_3^- \leftrightarrow NaHCO_{3,aq}$	0.162

Speciation in the aqueous phase

The demands for a satisfactorily solved system is that the solution is mass balanced and charge neutral. This is constrained by the equilibrium reactions listed in Table 1. Non-idealities of charged dissolves aqueous species is solved according to the Truesdell-Jones activity model [5], that is valid for up to 2M NaCl dominated solutions. Activity of CO₂ is calculated as a function of temperature according to the Drummond model [6], whereas activity of H₂O is calculated based on an expression in [7] which is quasi-consistent with the B-dot equation [8]. Further details on the aqueous speciation solver are presented in [9].

PHREEQC input values

One purpose of this study is to compare PHREEQC and ACCRETE calculations. PHREEQC uses partial pressures as input to simulations and assumes that fugacity equals the partial pressure. This results in poor estimates of solubility and carbon speciation at elevated pressures. This is solved in this study by estimating fugacity at various temperatures and pressures externally and use values as input to the PHREEQC speciation calculations. Fig. 1 shows PHREEQC values of solubility of CO₂ compared to data by Duan and Sun [1]. Including the fugacity coefficient $\phi(T, P)$ improves the results significantly, but it is still a

large discrepancy from the Duan and Sun data. By including a Poynting correction to the input data, this discrepancy is almost eliminated. Both of these corrections are included in the comparisons between ACCRETE and PHREEQC in the next section.

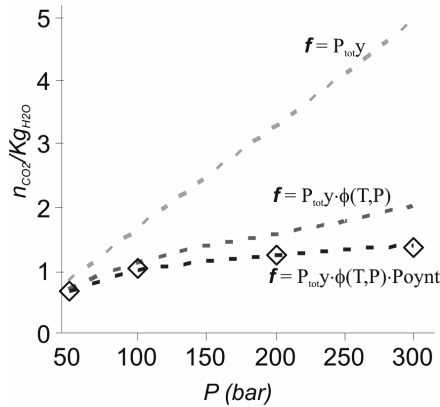


Fig. 1 PHREEQC estimations of CO_2 solubility (dashed line) compared to data by Duan and Sun [1] (diamonds). Large discrepancies are seen when fugacity is assumed equal to partial pressure. The result is improved by including a fugacity correction, and further improved by a poynting correction.

Results

Solubility of CO_2

The solubility of CO_2 is of major importance for estimating the storage potential of a system. On short timescale (a few years) solubility trapping totally dominates over mineral trapping, and it is detrimental for the movement and retention of supercritical or gaseous CO_2 . ACCRETE solubility estimations as a function of temperature, pressure and salinity are here compared to PHREEQC calculations and data by Duan and Sun listed in [1]. Fig. 2 shows the solubility calculations for freshwater (Fig. 2A) and a 1 molar NaCl solution (Fig. 2B) at 303 to 363 K and 50 to 300 bar CO_2 partial pressure. The figure suggests that ACCRETE and PHREEQC produce similar results, and that both are close to the reference data from Duan and Sun. The similarity between ACCRETE and PHREEQC is not surprising since the input fugacity and poynting corrections used in PHREEQC are identical to what is estimated in the ACCRETE code. Thus, in principle, the only differences between the calculations occur because of small differences in the Henrys law coefficient of CO_2 .

ACCRETE solubilities at temperatures above 333 K, especially for the 1 molar NaCl solutions, are lower than both PHREEQC and Duan and Sun. The discrepancy is most probably caused by the Henrys law coefficient polynomial used in ACCRETE which implicitly includes the salting out effect. The difference between ACCRETE solubility and Duan and Sun is however not considered dramatic within the temperature, pressure and salinity presented here.

Aqueous carbon speciation and pH

Speciation of aqueous carbon into bicarbonate and carbonate ions and mineral stabilities are both intimately connected to the pH of the solution. Accurate predictions of pH are of major importance since even small errors can lead to significant different mineral stabilities and mineral reaction directions.

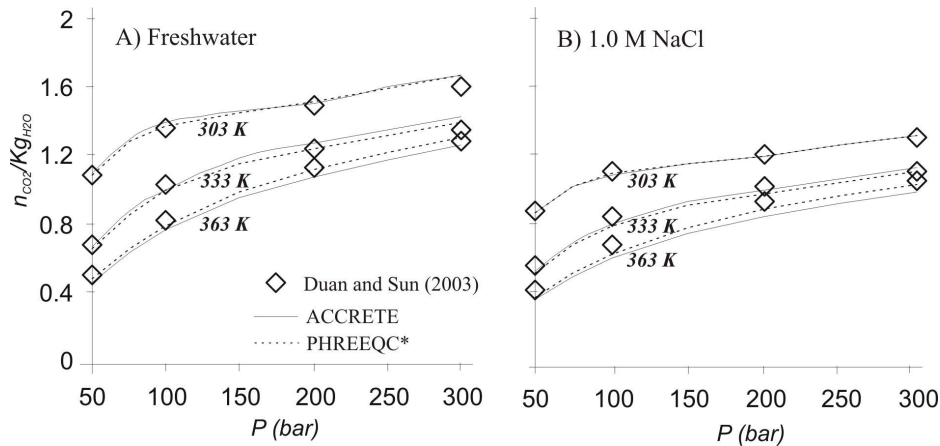


Fig. 2 Solubility of CO₂ in freshwater and 1 M NaCl aqueous solution. Diamonds, solid line and dashed line are data from Duan and Sun [1], ACCRETE, and PHREEQC respectively. The * indicates that input values of partial pressures are corrected for non-idealities caused by elevated temperatures and pressures.

Accurate pH estimations at elevated temperatures, CO₂ partial pressures, and salinities, demands activity models and thermodynamic data that are accurate at given conditions, as well as numerical solutions that satisfies charge- and mass balance demands. PHREEQC is known to predict aqueous speciation accurately for a large range of temperatures. Including corrections to the input CO₂ partial pressures should also ensure accurate pH predictions at elevated pressures. Fig. 3 shows ACCRETE and PHREEQC estimates of carbon speciation and pH at various temperatures and pressures. The drop in pH at elevated CO₂ partial pressures are shown in Fig. 3A for 303 and 363 K respectively. As *pH* drops, activity of CO_{2,aq} and bicarbonate increases accordingly, whereas the carbonate ion activity shows a slight decrease. The figure suggests that predictions by ACCRETE and PHREEQC to a large extent are comparable. The difference in pH at 363 K at all pressures is for example smaller than 0.01 pH unit. Differences between activities of carbon species are equally not significant.

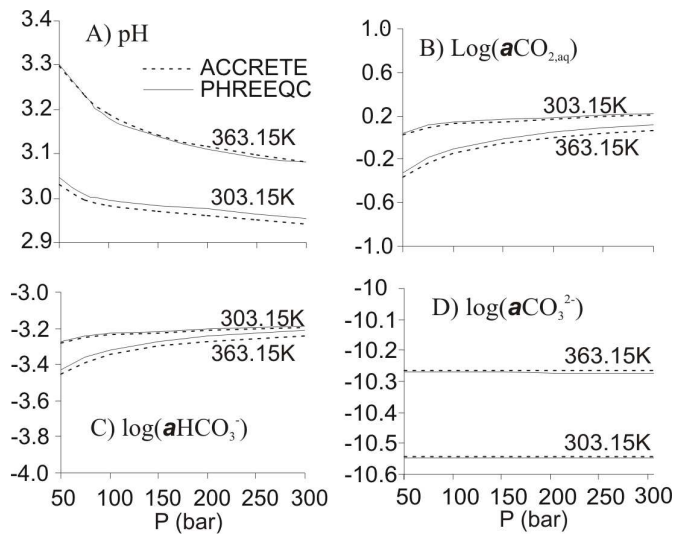


Fig. 3 ACCRETE and PHREEQC estimates of carbon speciation and pH at various temperatures and pressures.

Using the ACCRETE code in reactive transport simulations

The above sections shows that ACCRETE can accurately predict solubility of CO₂, carbon speciation, and pH at different temperatures, pressures and salinities. This section presents ACCRETE used as a geochemistry module coupled with the ATHENA thermal multiphase flow simulator in comprehensive reactive transport simulations including kinetically constrained mineral reactions. At present, 16 silicates, hydroxides and carbonates are included that may represent the primary mineralogy and possible secondary minerals that form in most CO₂ storage settings. Fig. 4 shows CO₂ saturation, pH and volume fraction of dawsonite in a 1000 years ATHENA reactive transport simulation. Initial mineralogy, temperature and pressure are comparable with the Utsira Sand at the Sleipner CO₂ injection facility [10].

The simulation shows that as CO₂ is injected, immiscible CO₂ rises buoyantly and accumulates beneath low-permeable intra-formation clayey horizons and beneath the top of the formation in topographic highs. CO₂ dissolves in the formation water and pH decreases to around 5.0 in equilibrium with calcite. The fast calcite reaction is considered as instrumental in buffering the pH drop during CO₂ storage. The acidic environment induces dissolution of primary minerals such as clinocllore-14A, daphnite-14A, and annite, which results in precipitation dominated by magnesite and siderite. Dawsonite precipitates only as a minor phase and dissolves at later stages of the simulations. Comparisons with various numerical studies show both similarities and dissimilarities which are suggested stems principally from differences in the use of primary and secondary forming minerals. Comparisons with natural systems also show similarities with features of general character, like formation of kaolinite from aluminosilicate dissolution, and dissolution of authigenic cements. The nature of the carbonate precipitates are strongly system dependent. A full report is available in [10].

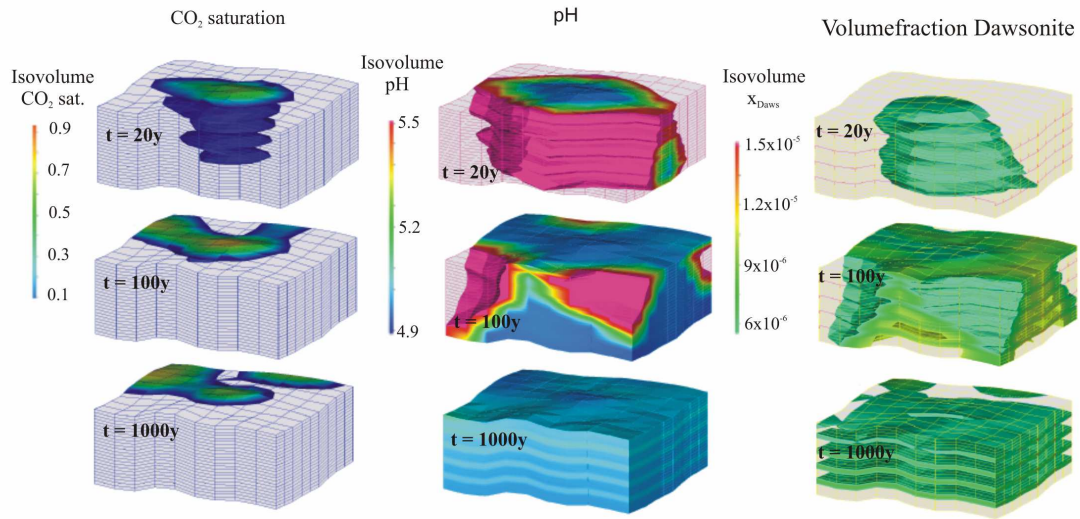


Fig. 4 3D reactive transport simulations using the ACCRETE geochemistry module coupled with the ATHENA thermal multiphase flow simulator.

Concluding remarks

To adequately solve geochemical interactions that occur during CO₂ storage the following three requirements should be satisfied: (1) accurate predictions of CO₂ solubility; (2) accurate predictions of carbon speciation; and (3) accurate predictions of kinetically constrained mineral reactions. Comparisons between data estimated by ACCRETE, Duan and Sun [1] and PHREEQC [2] suggest that CO₂ solubility is accurately estimated by ACCRETE. This is also true for the carbon speciation. Care has to be taken using PHREEQC since accurate predictions requires both a pre-calculated fugacity coefficient and a Poynting correction. With respect to mineral reactions, ACCRETE simulations compare qualitatively both with various numerical studies and with natural analogues.

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