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From CO₂ Transportation in Pipelines to Storage in Geological Formations: The Whole Picture of a Carbon Capture and Storage (CCS) Process with Chemical Thermodynamics

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Abstract

Climate change has been largely attributed to the amount of CO_2 released into the atmosphere, which has been continuously increasing. It is therefore vital to investigate the methods for eliminating the concentration of anthropic CO_2 from the atmosphere. The techniques developed for carbon dioxide capture and storage (CCS) are promising methods to tackle the challenge of global warming. A key step for having a secure CCS process is the transportation of captured CO_2 to storage sites i.e. subsurface geological reservoirs. In this regard, existence of suitable infrastructure equipment such as pipelines, with installed sufficient flow meters is necessary.

After CO_2 injection into the aquifers and having dissolved CO_2 in the aqueous phase, the pH of the solution decreases owing to the production of H^+ from carbonic acid in the aqueous phase. On the other hand, CO_2 solubility in brine would affect the performance of installed flow meters, due to density variations in the cargo fluid. Therefore, precise prediction of the CO_2 solubility in the aqueous phase is important for designing and increasing the efficiency of a CCS process. In this regard, it is critical to have access to enough experimental and theoretical information on the aforementioned phenomena to identify potential interactions among newly entered CO_2 molecules and the resident fluid/solid surface, while the influence of the other existing parameters e.g. ionic strength of brine needs to be taken into account.

The aim of this study is to illustrate how brine composition could affect the CO_2 solubility in the aqueous phase, geochemical trapping mechanisms, and rock-fluid interactions and induced pore structure alteration of the host rock. This will be achieved through a combination of thermodynamic modelling and experimental work on reservoir rock dissolution owing to the solubility of CO_2 in brine and the resultant pH variations. Herein, we have described and evaluated different equations of state (EoS) which utilise a robust thermodynamic basis for demonstrating the solubility of gas species in the aqueous phase which are integrated with Pitzer's theory for determination of the activity coefficients of the ionic species involved. This methodology proved to be able to describe the chemical equilibria of the ionic species in the aqueous phase under HPHT conditions and in systems of interest with presence of gas, which can lead to rock dissolution phenomenon through rock-acidic fluid interactions. Generally, good agreement between predictions and experimental results are observed, and the thermodynamic modelling results could explain one of the dominating drivers of the rock dissolution phenomenon; pH alteration.

Introduction

The main goal of Carbon Capture and Storage (CCS) projects is reducing the amount of CO_2 in the atmosphere by employing different techniques for capturing the carbon dioxide with subsequent permanent storage in secure subsurface formations e.g. deep saline aquifers and depleted oil and gas reservoirs [1], [2]. Optimising the performance of CCS projects to remove

economic obstacles, is one of the priorities for researchers against the usual costly CCS technologies [3]. The storage of CO_2 in deep saline aquifers has been recognised as a promising method for mitigating atmospheric CO_2. The existence of two trapping mechanisms such as solubility and mineralisation of injected CO_2 make the subsurface reservoirs a safe place for long-term maintenance of captured CO_2. The mechanism of solubility-trapping consists of the dissolution of newly entered CO_2 after being in contact with the residence fluid [4]. The dissolved CO_2 will turn to carbonic acid and release protons (H^+) which reduces the pH of the formation water and accelerates the reactivity of the aqueous phase. Due to the rock-fluid interactions, the pH of the solution will vary as the result of the dominant carbonic specie i.e. HCO_3^- (buffer/neutral pH) and CO_3^{2-} (basic pH). Therefore, the injection of CO_2 will disrupt the equilibrium between the resident phases and introduce new hydrogeochemical and mechanical reactions [5]. The determination of pH is critical when considering the properties of the fluid, due to the presence of salts in the formation fluid. The alteration of pH can also introduce new reactions, such as corrosion of the metallic equipment installed on downstream facilities on well head and dissolution and precipitation of reservoir rock and scaling inside the transporting pipelines [6]. Therefore, the key parameters in a CCS process are CO_2 solubility at the HPHT condition of subsurface storage sites, induced pH variations, phase behaviour of the CO_2-brine system and thermophysical properties of the fluid at the reservoir conditions for precise and efficient designing of the CO_2 storage process. The precise thermodynamic modelling of CO_2 solubility is helpful for optimising the design, improvement and propagation of novel CCS methodologies and it is more critical for the methods that the mass transfer rate between gas and liquid phases is determined by assuming equilibrium conditions among the elements in the system.

In this paper, we have used various equations of state (EoS) to predict the solubility of CO_2 in water and induced pH variations at a wide range of pressures and temperatures We have searched for respective experimental data for modifying and validating the thermodynamic models used to calculate the gas solubility in aqueous phase and induced pH changes. The existence of different cations (Na^+, K^+, Ca^+ and Mg^+) in the formation brine can change the thermodynamic behaviour of the fluid phases from the estimated conditions with no salt, making the system more complex for thermodynamic modelling. Among the dissolved species, Na^+ and Cl^- are the most abundant elements found in the aqueous phase of deep saline aquifers. Therefore, in this research work the synthesised formation brines using NaCl have been studied, and the condition of geological storage has been simulated with respect to the CO_2 phase behaviour and pH values using a simplified mixture of NaCl-CO_2-water. To the best of the authors' knowledge, no solidarity equation of state has been reported in the literature regarding the most effective EoS for transporting and compressing CO_2. Since there is a gap according to deficiency in the assessments of model predictions compared with experimental data, the aim of this work is to propose an appropriate EoS for studied systems. Finally, the modelling results have been compared with the rock dissolution experimental results due to the CO_2 solubility in the brine and induced pH alteration, in order to understand the potential drivers behind the rock dissolution phenomenon during a CO_2 sequestration process.

Experimental Methods and Thermodynamic Modelling

The experimental data of the solubility of CO_2 in water and NaCl brine at different ionic strength in the literature [4], [7] were used to evaluate the solubility predictions using cubic, and statistical associating fluid theory (SAFT)-based equations of state. In this work, Soave-Redlich-Kwong (SRK) [8], Peng-Robinson Cubic Plus Association [9], and Perturbed-Chain SAFT (PC-SAFT) [10] equations of state were employed to predict the CO_2 solubilities in the

aqueous phase at different pressure and temperature conditions. The details of each equation of state have been presented in the corresponding reference. In this study the PR-CPA (as one of the most appropriate nominees for determining the solubility of CO_2 molecules in the aqueous phase at HPHT conditions) was integrated with the well-known Pitzer's equations [11] for determination of the deviations from ideality of each ionic species in the liquid phase and dissolved CO_2-induced pH alterations in the studied systems.

The basic equation utilised to determine the pH is expressed as:

$$pH = -log_{10}(a_{H^+}) = -log_{10}(m_{H^+}) - log_{10}(\gamma_{H^+}) \tag{1}$$

Where a_{H^+} is the activity in molal concentration, m_{H^+} (mol.kg^{-1}) is the molal concentration, and γ_{H^+} (dimensionless) is the activity coefficient of the hydrogen ions. For investigating the effect of ionic strength on Berea sandstone reactivity according to the discussed CO_2 solubility and induced pH changes, two brines with two different salinities were synthesised to be representative of low and high salinity formation brine. Two analytical techniques, which are micro-Computed Tomography (μ-CT) scanner and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), have been employed to assess rock and fluid-composition alterations before and after each experiment.

Results and Discussion

The experimental and predicted solubility values of carbon dioxide in pure water, 1.13 m NaCl, and 3 m NaCl at two temperatures and as a function of pressure are presented in Figure 1. The solubilities at ~323.1 K and ~373 K are plotted versus pressure in figure 1a and 1b, respectively, with the experimental data of Koschel et al. [4], and Chabab et al. [7]. We have also shown the predicted values obtained from three SRK, PR-CPA, and PC-SAFT equations of state. At two temperatures, the solubility of CO_2 sharply increased with increasing pressure, up to the vicinity of the critical pressure of pure CO_2. Above the 10 MPa, the CO_2 solubility in pure water still increases with pressure but the rate is much slower. The CO_2 solubility in water at ~373 K is lower than 323.1 K. This is due to the exothermic process of CO_2 dissolution in water (H$_{sol}$ < 0) in the given temperature range. The discrepancy in CO_2 solubility at the two temperatures is smaller with increasing pressure. As an example, the CO_2 solubility in water at 373 K and 5 MPa is ~43 % lower compared to the solubility value at the same pressure and ~323.1 K whilst only ~33% and 10% at 10 and 20MPa, respectively. As can be seen, PC-SAFT and PR-CPA EoS could successfully predict both the trend and solubility values at given pressure and temperature conditions. PR-CPA performs marginally better than PC-SAFT for the CO_2-water binary mixture.

The experimental and modelled CO_2 solubilities in aqueous solutions of 1.13 m and 3 m NaCl at the same temperatures and pressures as the previous case of binary mixture were also presented in figure 1. The CO_2 solubility in the NaCl brine solution reduces with the increasing ionic strength of the aqueous phase owing to the so-called salting out effect. Both our modelling results and the literature experimental data at temperatures of ~323.1 K and ~373 K and in the pressure range between 5 and 20 MPa depict that there is no remarkable temperature and pressure dependence of the salting-out effect in the studied realm. The predictions of SRK, PR-CPA, and PC-SAFT were compared with the experimental data for the H_2O-CO_2-NaCl system at different ionic strengths. In order to investigate the effects of pressure, temperature, and brine ionic strength on pH values, the existing data in the open literature [12], [13] were collected. The three EoS are in good agreement with the trend of the experimental data and have better solubility prediction performance at lower pressures. Figure 1c depicts the experimental and

modelling results of the pH values for two isotherms for the CO_2-H_2O-NaCl systems with different ionic strengths (1 m and 3m NaCl) in the temperature range of 293.15–323.15 K and pressures up to ~15 MPa. As can be seen, for all studied isotherms/aqueous phase ionic strengths, the pH value reduces substantially with pressure increment whilst the operating pressure is less than 4 MPa. This decrease in pH values is less for pressures higher than 4 MPa. This trend is due to higher alteration of the CO_2 solubility in the aqueous phase at low pressures. Figure 1c clearly denotes that the salinity increased from 1 m to 3 m, results in a profound pH decrease in the acidified brine over the whole range of pressure and isotherm conditions.
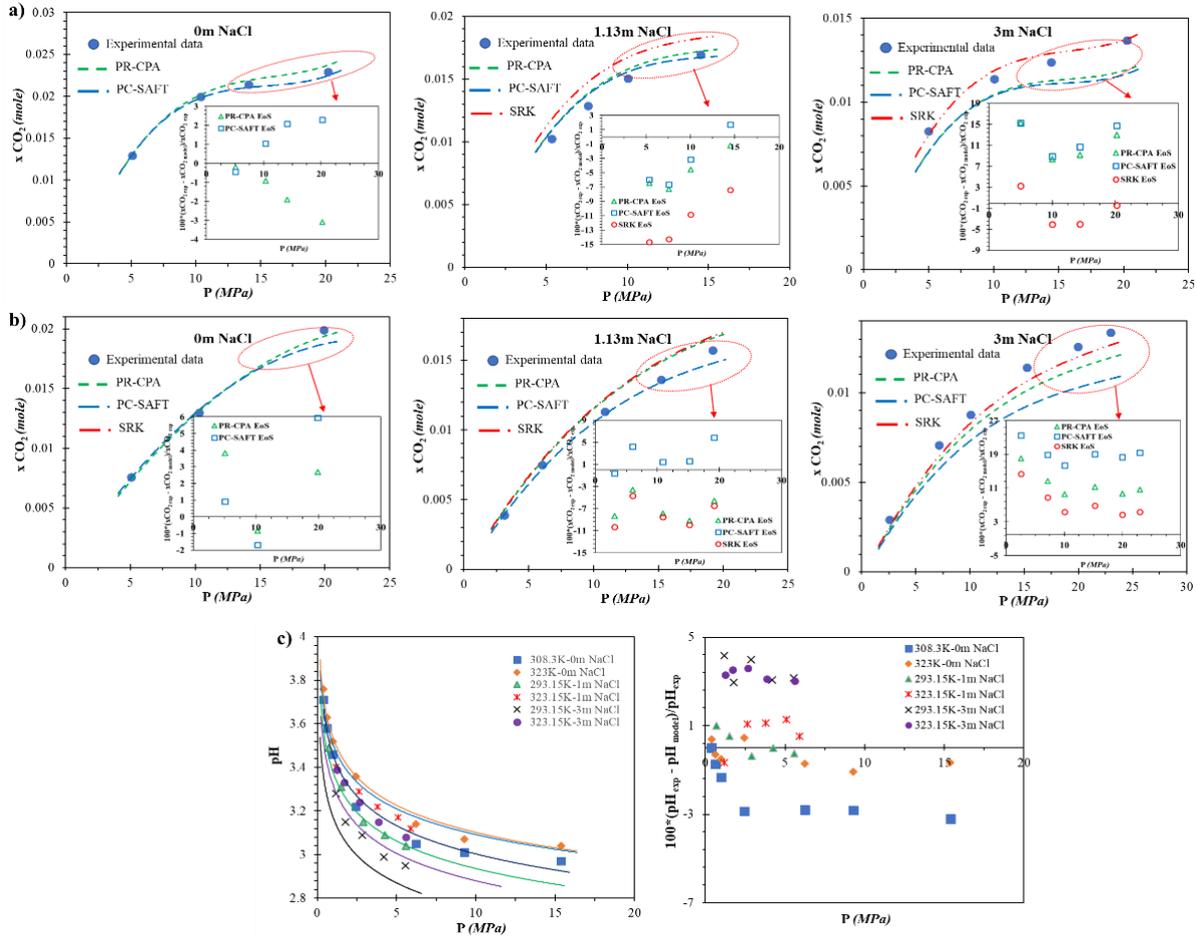
Figure 1. *Modelling and experimental results of CO_2 solubilities in aqueous phase with various ionic strengths at different pressures and temperatures of a) 323.1 K, and b) 373 K. Filled blue circles represent the experimental data from the literature [4], [7]; c) pH values of CO_2 saturated solutions versus pressure at different temperatures for the CO_2-H_2O and CO_2-H_2O-NaCl systems. Solid lines are the predictions from the presented model. Symbols are experimental data [12], [13] from the literature.*

As depicted in figure 1a and 1b, the solubility of CO_2 reduces with the increase of brine ionic strength, however, the hydrogen ion activity coefficient (γ_{H+}) considerably increases with increasing ionic strength leading to the pH value reduction. The pH predictions determined by our integrated PR-CPA-Pitzer model were evaluated against the experimental data which have also been presented in figure 1c. It can be observed that the model-predicted pH values have a good agreement with the experimental data at various isotherms, ionic strengths, and pressures up to 15 MPa. Porosity analysis was employed on reconstructed 3D geometry of core plugs with similar dimensions (5 mm×12 mm). As illustrated in figure 2, the pore spaces increased

in contact with test fluids at HPHT, while higher salinity (figure 2a, b) enlarges the pore spaces more than the low salinity brine (figure 2c, d). The results from ICP-OES also confirmed that more ions were extracted from the core sample when in contact with high-salinity fluid in comparison with low-salinity brine. Therefore, higher ionic strength and the related induced lower pH due to the higher hydrogen ion activity coefficient (figure 1c), intensify the rock-fluid reactivity.
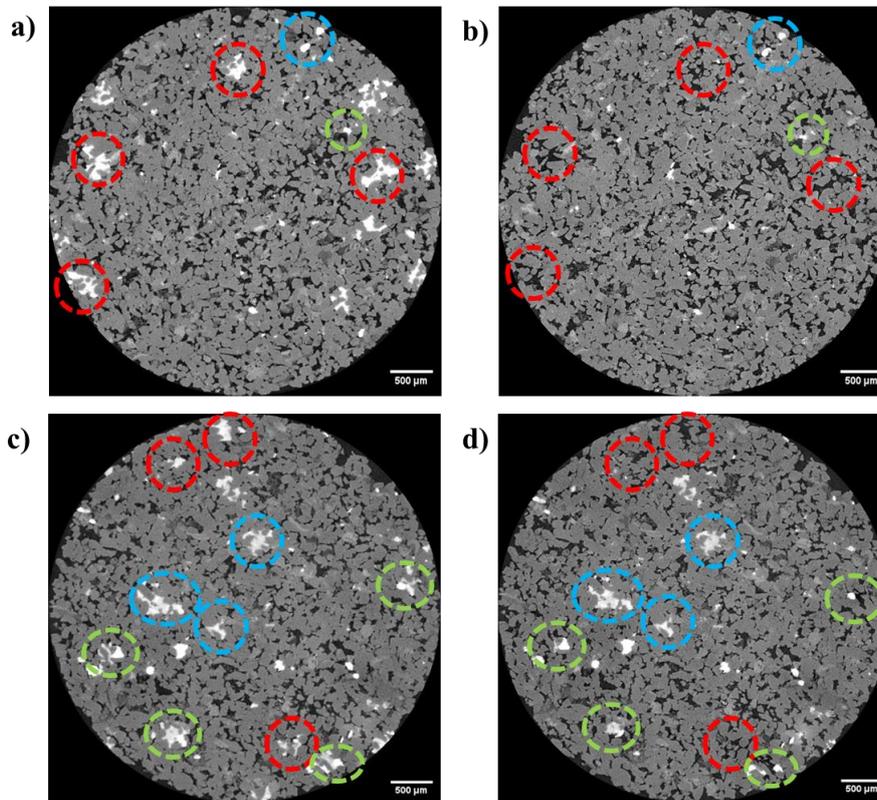
Figure 2. *a) Cross sections from original grey-scale tomogram (white: iron-rich minerals, light grey: carbonate minerals, dark grey: silicate minerals and black: pore spaces). The images show a) the initial state and b) the final state after experiment with high salinity brine, c) initial state and d) final state after experiment with low salinity brine. The red, green and blue dashed circles are highlighting the areas where carbonate minerals are dissolved completely, dissolved partially and remained intact, respectively.*

Conclusions

Good agreement was achieved between the literature experimental data and some EoS prediction values for both pH and CO_2 solubility in the aqueous phase. It was illustrated that the pH values of all the studied systems begins to suppress with pressure increment at each isotherm. According to the thermodynamic modelling results, this decrease is particularly evident while the pressure is less than 4 MPa, and the pH value begins decreasing subtly at pressures higher than 4 MPa. These observations have been explained by the alteration in the CO_2 solubility in the aqueous phase at various pressures. The solubility of CO_2 in the aqueous phase increases with an increase in pressure but decreases with increasing temperature. It was noted that the pH of CO_2-saturated brines reduces with an increment in the brine's ionic strengths at constant pressure and temperature conditions. Our modelling results indicate a significant salting-out effect in NaCl solutions which is consistent with the experimental results

of CO_2 solubility measurements in the CO_2-H_2O-NaCl systems. Moreover, higher ionic strength boosts the rock-fluid interactions through increased rock dissolution owing to lower pH values. This is in thorough agreement with thermodynamic modelling results obtained.

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