Introduction
The main goal of a Carbon Capture and Storage (CCS) projects is deducting the amount of CO₂ in atmosphere via employing different techniques for capturing the carbon dioxide and then permanent storing in secure subsurface formations e.g. deep saline aquifers and depleted oil and gas reservoirs [1], [2]. Optimising the performance of CCS projects is one of the priorities for researchers against the ordinary costly CCS technologies [3] to remove economical obstacles. The storage of CO₂ in deep saline aquifers has been recognised as a promising method for mitigating atmospheric CO₂. The existence of two trapping mechanisms such as solubility and mineralisation of injected CO₂ make the subsurface reservoirs a safe place for long-term maintenance of captured CO₂. The mechanism of solubility trapping consists of dissolution of newly entered CO₂ after being contacted with the residence fluid [4]. The dissolved CO₂ will turn to carabolic acid and release proton (H⁺) which drops down the pH of the formation water and accelerate 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. HCO₃⁻ (buffer/neural pH) and CO₃²⁻ (basic pH). Therefore, the injection of CO₂ will disrupt the equilibrium condition between the resident phases and introduce new hydrogeochemical and mechanical reactions [5]. Different salts are also present in formation fluid, the determination of the pH is more critical for determining the properties of the fluid. The alteration of pH can introduce new reactions such as corrosion of the metallic equipment installed on downstream facilities on well head, dissolution and precipitation of reservoir rock and scaling inside the transporting pipelines [6]. Therefore, the key parameters in a CCS process are CO₂ solubility at HPHT condition of subsurface storage sites, induced pH variations, phase behaviour of the CO₂-brine system and thermophysical properties of the fluid at the reservoir conditions for precise and efficient designing of CO₂ storage process. The precise thermodynamic modelling of CO₂ 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 condition among elements in the system.

In this paper, we have used various equations of state (EoS) to predict the solubility of CO₂ in water and induced pH variations at wide range of pressure and temperature using. We have searched for respective experimental data for modifying and validating the thermodynamic models for calculating the gas solubility in aqueous phase and induced pH changes. The existence of different cations (Na⁺, K⁺, Ca⁺ and Mg⁺) at formation brine can change the thermodynamic behaviour of fluid phases from the estimated condition with no salt and make the system more complex for thermodynamic modelling. Among the dissolved species Na⁺ and Cl⁻ are the most abundant elements found in aqueous phase of deep saline aquifiers. Therefore, in this research work the synthesised formations brines using NaCl have been studied, and the condition of geological storage has been simulated with respect to the CO₂ phase behaviour and pH values using simplified mixture of NaCl-CO₂-water. To the best of authors’ knowledge, no solarity equation of state has been reported in the literature regarding the most effective EoS for transporting and compressing CO₂. Since there is a gap according to deficiency in assessments of model predictions comparing with experimental data, the aim of this work is to propose an appropriate EoS for studied systems. At the end, the modelling results have been compared with the rock dissolution experimental results due to the CO₂ solubility in the brine and induced pH alteration in order to understand the potential drivers behind the rock dissolution phenomenon during a CO₂ sequestration process.

Experimental Methods and Thermodynamic Modelling
The experimental data of the solubility of CO₂ 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 CO₂ 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 CO₂ molecules in the aqueous phase at HPHT conditions was integrated with the well-known Pitzer’s
equations [11] for determination of the deviations to the 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:

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

Where $a_{H^+}$ is the activity in molal concentration, $m_{H^+}$ (mol.kg$^{-1}$) is the molar concentration, and $\gamma_{H^+}$ (dimensionless) is the hydrogen ions activity coefficient. 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 regarding assessments of 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, 1.13m NaCl, and 3m NaCl at two temperatures and as a function of pressure are presented in Figure 1. The solubilities at ~323.1K and ~373 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$_2$ was sharply incremented 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 increments with pressure but the alteration is much slower. The CO$_2$ solubility in water at ~373K is lower compared to at 323.1 K. This is because of 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 reducing with increasing pressure. As an example, the CO$_2$ solubility in water at 373K and 5MPa is ~43% lower compared to the solubility value at the same pressure and ~323.1K 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 has a bit better performance compared to PC-SAFT for the CO$_2$-water binary mixture.

The experimental and modelled CO$_2$ solubilities in aqueous solutions of 1.13 and 3m 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 NaCl brine solution reduces with incrementing 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 ~323.1K and ~373K 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 done by SRK, PR-CPA, and PC-SAFT were compared with the experimental data for the H$_2$O-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 predictions performance at lower pressures. Figure 1c depicts the experimental and modelling results of the pH values for two isotherms for the CO$_2$-H$_2$O-NaCl systems with different ionic strengths (1 and 3m NaCl) in the temperature range of 293.15–323.15K and pressures up to ~15MPa. As can be seen, for all studied isotherms/aqueous phase ionic strengths the pH value reduces keenly with pressure increment whilst the operating pressure is less than 4MPa. This decrease in pH values is less for pressures higher than 4MPa. 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 increment from 1m to 3m 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 CO₂ solubilities in aqueous phase with various ionic strengths at different pressures and temperatures of a) 323.1K, and b) 373K. Filled blue circles represent the experimental data from the literature [4], [7]; c) pH values of CO₂ saturated solutions versus pressure at different temperatures for the CO₂-H₂O and CO₂-H₂O-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 CO₂ reduces with the increase of brine ionic strength, however, the hydrogen ion activity coefficient ($\gamma_{H^+}$) considerably increments with the increase of ionic strength which lead 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 predicted pH values by the model have a good agreement with the experimental data at various isotherms, ionic strengths, and pressures up to 15MPa. Porosity analysis were employed on reconstructed 3D geometry of core plugs with similar dimensions (1mm×1mm). As illustrated in figure 2a, the volume of the pore spaces increased by contacting with test fluids at HPHT while higher salinity enlarge the pore spaces more than low salinity brine. The results from ICP-OES (figure 2b) also confirmed that more ions were extracted from the core sample in contact with high salinity fluid in comparison with low salinity brine. Therefore, both parameters of higher ionic strength and induced lower pH due to the higher hydrogen ion activity coefficient (figure 1c) intensify the rock-fluid reactivity.
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 keen while the pressure is less than 4MPa, and pH value begins decreasing gently at pressures higher than 4MPa. 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 pressure increase while decreases with temperature increment. It was denoted that the pH of CO$_2$-saturated brines reduces with an increment in the brine’s ionic strengths at the 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$_2$O-NaCl systems. Moreover, higher ionic strength boost the rock-fluid interactions by introducing more rock dissolution owing to lower pH values which is in thorough agreement with thermodynamic modelling results.

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 keen while the pressure is less than 4MPa, and pH value begins decreasing gently at pressures higher than 4MPa. 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 pressure increase while decreases with temperature increment. It was denoted that the pH of CO$_2$-saturated brines reduces with an increment in the brine’s ionic strengths at the 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$_2$O-NaCl systems. Moreover, higher ionic strength boost the rock-fluid interactions by introducing more rock dissolution owing to lower pH values which is in thorough agreement with thermodynamic modelling results.

References