IOP Conf. Series: Materials Science and Engineering **358** (2018) 012013 doi:10.1088/1757-899X/358/1/012013

Semi-Empirical Model to Estimate the Solubility of CO_2 NaCl Brine in Conditions Representative of CO_2 Sequestration

E Mohammadian*[1], H Hamidi[2] and A Azdarpour [3]
[1] Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 UiTM, Shah Alam, Selangor, Malaysia
[2]383 Fraser Noble Building, School of Engineering, King's College, University of Aberdeen, Scotland, UK
[3] Department of Petroleum Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran

.

Erfan.723@gmail.com

Abstract. CO_2 sequestration is considered as one of the most anticipated methods to mitigate CO_2 concentration in the atmosphere. Solubility mechanism is one of the most important and sophisticated mechanisms by which CO_2 is rendered immobile while it is being injected into aquifers. A semi-empirical, easy to use model was developed to calculate the solubility of CO_2 in NaCl brines with thermodynamic conditions (pressure, temperature) and salinity gradients representative CO_2 sequestration in the Malay basin. The model was compared to the previous more sophisticated models and a good consistency was found among the data obtained using the two models. A Sensitivity analysis was also conducted on the model to test its performance beyond its limits.

1. Introduction

Burning fossil fuels has released enormous amounts of greenhouse gases in the atmosphere since the industrial revolution. The greenhouse gases are the main reason behind the global warming [1]. Carbon dioxide (CO_2) sequestration in the aquifers is one of the most anticipated methods to mitigate CO_2 concentration in the atmosphere. CO_2 sequestration potentially provides around 25 % of the required mitigation to global emissions, which can delay global warming to an acceptable extent If successfully conducted, CO2 may be safely sequestrated in depleted (or active) saline aquifers, un-minable coal beds, oil and gas reservoirs. [1-2] Due to known geological formation and existence of seal traps, CO_2 may be more safely sequestrated in depleted oil and gas reservoirs as compared to saline aquifers and coal bed methane reservoirs. On the other hand, the abundance and higher storage capacity are two major motivations for sequestration of CO_2 in saline aquifers. [3]

There are four main mechanisms of sequestration, which contribute in rendering the injected carbon dioxide immobile: structural trapping, residual phase trapping mineralization and dissolution of and carbon dioxide in formation brine. Mineral trapping is reaction of CO_2 with minerals existed in rock to form stable components i.e. carbonates and almino-silicate. The carbon dioxide secured by mineralization mechanism is proven to be the safest in terms of releasing back to atmosphere. [4] However the time scales of the reaction is known to be very long [1]. Therefore the attempt has been undertaken to accelerate the mineralization reactions.The importance of solubility mechanism is that it could be manipulated to increase the sequestration efficiency. Besides, in the newer methods such as surface mixing, solubility of CO_2 in water (or brine) is the key parameter that could increase the CO_2 mitigation efficiency. For CO_2 sequestration operations on the other hand, the importance of solubility mechanisms is that rate under which CO_2 is secured using solubility mechanism are higher than those of mineralization. [2,4] So far, there have been numerous studies that experimentally investigated effects of various parameters on the solubility of CO_2 in brine in a variety of conditions [5]. There are plenty of experimental and theoretical studies regarding the future implementation of CO_2 sequestration in the areas such as North Sea and the U.S. However, in case of Malay basin, there is a lack of experimental and modelling studies on CO_2 sequestration. Since Malaysia has been one of the countries that is a member of the Kyoto protocol [6] and therefore taking measures to mitigate its produced CO_2 in inevitable.

2. Model Development

For sequestration purposes, CO_2 is injected as the supercritical fluid, i.e. at pressures above 72.9 atm, so the risk of leakage is minimized [7]. There are limited modelling studies by which solubility of CO_2 in brine could be estimated in conditions in favor of CO_2 sequestration, Moreover, some of the previous models use sophisticated techniques and lots of assumptions. This study seeks to propose an empirical model to describe CO_2 solubility in conditions representative of Malay basin. The formation brine composition and pressure and temperature gradients were chosen in an order to achieve that objective. The model data were obtained from the various experiments conducted in the author's previous work [8]. The experiments were conducted in an autoclave reactor up to 300 atm of pressure. The detailed about experimental setup and procedure could be found in the authors' previous work [8]. Figure 1 shows the parameters that were studied in the experimental phase.

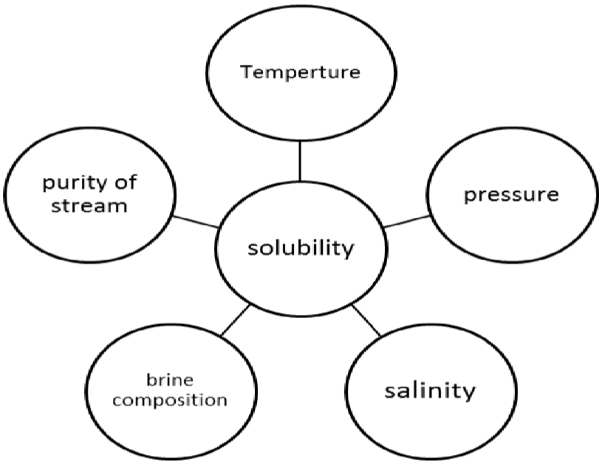

Figure 1. The parameters that affect the solubility were experimentally investigated

Once the experimental phase completed, the outliers (data with irrationally high or low values) were identified and removed using static data analysis software (such as SPSS™ 18). The latter was done using z-score method. Once the outliers were removed, the model can be developed by using various regression techniques according to the number of independent variables (pressure, temperature, salinity and purity of the stream) and the changes of dependent variable (solubility) with that independent variable. The correlation between the dependent and independent variable can be shown as follows:

$$x = f(P, T, S, F) \qquad [1]$$

In the above correlation, x is the solubility of CO_2 in brine, P is the pressure, T is the temperature, S represents the salinity of the brine and F represents the purity of stream. The range of salinity is in this study was (1000, 10,000, and 15,000 ppm). In order to develop models, nonlinear regression was used. In non-linear regression analysis, the observational (experimental) data were modelled by a function, which is the combination (nonlinear) of the model parameters and depends on a number of independent variables. In order to do the regression, a raw equation was defined together with number of constants. The data are fitted by a method of consecutive iterations to the point where the best model was obtained. Various models have been investigated and one with the highest R2 (goodness of the fitting line or curve) was chosen as the proper model for the solubility (dependent variable). The model than checked with the experimental data of author's previous work [8] to verify its performance. The developed model is able to predict the solubility of CO_2 in water in a variety of conditions. Once the model was developed, it was tested beyond its range of P-T-s and compared to the previous models to test its performance. Figure 2 shows the flowchart of model development.

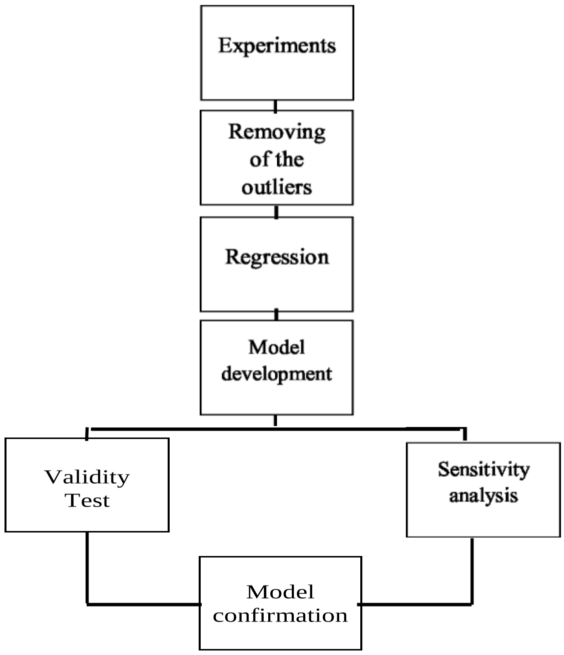

Figure 2. Model development flowchart

2.1. Model preparation

The model was developed through several attempts of regression solubility data with those of pressure, temperature, salinity and purity of stream. The purity of the stream was added to investigate the option of co-injection of other gases with CO_2 stream (Such as N_2 and Ar). Due to several technical and economic reasons co-injection of impurities with CO_2 stream could be of a great significance [9]. Once the various models were tested, the one with the highest goodness of the fit was chosen. The R_2 of the following model is 98.3%.

$$x = \left(\left[\left(c + \frac{RaT^2}{Pb} \right) + 1 \right]^{-1} - (dS) \right) \times F \, . \, g \qquad [2]$$

where x is the solubility of CO_2 in brine in mol/kg, R is the universal constant for gases (82.023 cm3.atm. K^{-1} .mol^{-1}), T is the temperature in Kelvin, P is the pressure in atm, S is the salinity of brine, in this case NaCl is the only salt present in the brine, in wt% , F is purity of the stream based on N2 content in volume percent (for a stream with 100% CO_2 the value is 1 and for 90% CO_2 +10% N_2 the value is 0.9) the value is *a, b, c, d,* and *g* are regression constants as shown in Table 1. Unlike the few available models, this model is an empirical, simple to use method as it has been solely obtained based on the statistical analysis of the experimental data. The previous models are more complicated and calculate the solubility by aid of parameters such entropy, fugacity at any pressure, temperature and salinity of interest etc [11].

Table 1. Parameters estimated from SPSS (R^2 = 0.983)

Parameter	Estimate
a	0.063
b	745.515
c	6.882
d	0.005

2.2. Model verification

All of the tables, images and figures should be centered. Figures and images should be numbered together (Figure 1) and figure definitions should be placed under the figure or image; as for the tables, they should also be numbered (Table 1) and the table header should be placed at the top of the chart. Table, image and figure headers should be written with upper case initial letters, bold and should be centered. References (if any) of the tables, figures and images should be presented just in the tables, figures and images in the form of author surname and publication date. In order to test the integrity of this empirical model, first it was verified using experimental data. Once verified, the outcomes were compared with previous models [10] at the same conditions to ensure the applicability of models developed in this research. Figure 3 illustrates the comparison between solubility data of 100% pure CO_2 stream obtained using experiments and models developed above in 10000 ppm NaCl brine, at 353 and 373 K. Figure 4 illustrates the Comparison between the solubility values of stream containing 95% CO_2+ 5% N2 in a 15,000 ppm NaCl brine at a temperature of 333 K obtained in the experiments to those obtained using the model.As it can be seen from Figures 3 and 4, there is a very good agreement between the experimental and model outcomes at both of the temperature series and different purities of the stream. The latter was also apparent from the very high coefficient of correlation, R squared, of 98.3% for NaCl Brine obtained from non-linear regression using SPSS software. It is useful to compare the solubility values obtained from the current model to previous models. Very few models are available in a wide range of pressure, temperature and salinity comparable to those of this study. One of the models comparable is the one developed by Duan and Sun [10] which covers solubility of CO_2 in seawater as well as brine saturated with various types of salts. Thus, it is among the most comprehensive models developed to date. Figure 5 illustrates solubility of CO_2 in brine obtained from Duan and Sun [10] and that of calculated in this research. It can be seen that at both temperature series of 353 K, there is a very good agreement with the model developed by Duan and Sun [10] and that of this study. At 353°K the values calculated using the two models are more identical, however just like the previous case, at higher pressures, 190 bar as an example, the highest difference in solubility can be observed to be 1.9 %.

2.3. Model limitations

This section presents a sensitivity analysis, that was conducted to test the model performance beyond its allowable range of function i.e. pressure range of 2-210 atm, 298-373 ºK and TDS of 0- 1.5 wt%. The validity of the model beyond it limits, i.e. the solubility at higher temperature, pressure and salinity was calculated using the model developed in this study (Mohammadian’s model) and was compared to the literature. Table 1 summarizes the “off-limits” calculation of the current model, in contrast with those calculated from Duan and Suns’ (2003) model. In the first step, the solubility values are calculated at 333 °K, from 220 to 400 atm. The Current model works fine beyond its pressure limits with a negligible error of less than 3% at pressures up to 500 atm. It can be seen that the error is increased at higher pressures. Considering normal gradient of 0.44 psi/ft in Malay basin, pressure of 500 atm, represents a formation with Depths more than 16700 feet which is considered ultra-deep formation. Therefore the application of CO_2 sequestration method in ultra-deep formation will be challenging and would requires all-inclusive understanding from the technical and economical point of view.

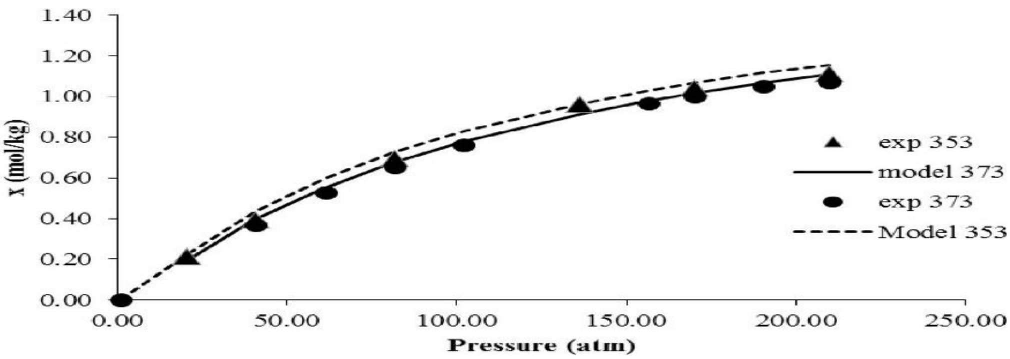

Figure 3. Model and experimental data of solubility of pure CO_2 in brine of 10,000 ppm at 353 and 373 K.

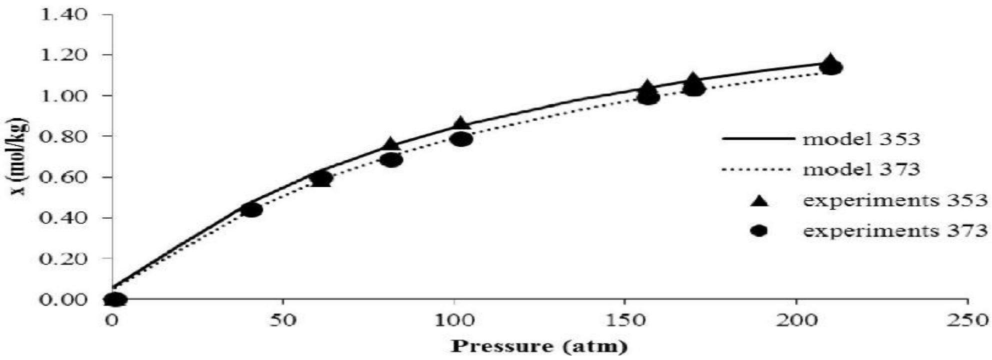

Figure 4. Model and experimental data of solubility of 95% CO_2 +5 N_2% in brine of 1000 ppm at 353 and 373 K.

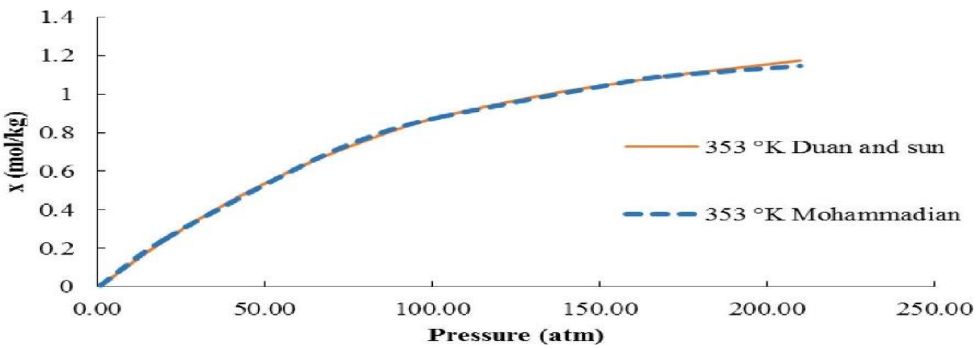

Figure 5 Comparison of solubility obtained from the current model with those of Duan and Sun (2003).

However, using the model beyond its temperature range produces rather larger errors (up to 41%). The latter is due to the inversion of temperature effect on solubility, which occurs at high pressures. This effect causes a rather unexpected increase in the solubility of CO_2 as temperature increases and has been reported by some of the previous researchers (Duan and Sun, 2003; Duan *et* al., 2006; Tong *et* al., 2013) without any explanation of the cause. The reason that model is not able to detect this effect, may be due to the fact that the model was developed based on experimental data obtained at lower temperature ranges. Therefore, the effect was not observed from experimental data gained in this research. Testing the model beyond its salinity limits generated errors up to 7%. Although the tolerance for error is usually around 5%, it is still acceptable to use the model out of its salinity range which is 0-15000 ppm. Moreover, the model could not be tested in various conditions of impurity in the stream as to date, to the authors' knowledge, there is no model or experimental data on effects of impurities in the stream and therefore there is no benchmark to test the current model with. To sum up, within an acceptable range of error, the model works fine, even at pressures and brine salinities beyond its scope. However care should be taken in using the model at temperatures higher than its limit i.e. 373 K as significant errors can be encountered.

3. Conclusions

In this research an empirical correlation was developed based on the experiments on the solubility of CO_2 in NaCl brines. The effects of pressure, temperature, salinity and purity of CO_2 stream was considered as independent variable whereas CO_2 solubility was the dependent variable in the model. The novelty of the model is that, it is very simple to use and accurate in its range of application and to some extends beyond them (depending on the parameter). The model was compared to the previous most widely-known models of literature and a good consistency was observed.

Referances

[1] Intergovernmental Panel on Climate Change 2003. Good Practice Guidance for Land Use, Land-use Change and Forestry. The IPCC good practice guidance for LULUCF.
[2] Bachu S S 2005 Special report on carbon dioxide capture and storage. *IPCC–Intergovernmental Panel on Climate Change*.
[3] Godec M L, Kuuskraa V A and Dipietro P 2013 *J.of Energy and Fuels*, **27** (8) 4183–4189
[4] Blyton, C A Bryant S L 2013 *Chemical Engineering Science* **101** 461–469
[5] Hou S, Maitland G C, Trusler J P 2013 *J. of Supercritical Fluids* **73** 87– 96
[6] United Nation Framework Convention on Climate Change 2002. Koyoto protocol reference manual
[7] Zhao, X and Liao X 2012 *Journal of Energy and Fuels* **26** (8) 5350–5354
[8] Mohammadian, E, Hamidi H, Azdarpour A, Asadualah M and Junin, R 2015 *Journal of Chemical & Engineering Data* **60** (7)
[9] Thodla, R, Francois, A, and Sridhar, N 2009. Materials Performance. In Supercritical CO_2 Environments. NACE conference. Presented in Las Vegas, USA. No. 09255
[10] Duan Z and Sun R 2003 *Chemical Geology* **193** 257– 27
[11] Mao S, Zhang, D, Li Y and Liu N 2013 *Chemical Geology* **347** Pages 43-58