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Improved Solubility Model for Pure Gas and Binary Mixture of CO_2-H_2S in Water: A Geothermal Case Study with Total Reinjection

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Abstract: Geothermal energy is acknowledged globally as a renewable resource, which, unlike solar, wind or wave energy, can be continuously exploited. The geothermal fluids usually have some acid gas content, which needs to be precisely taken into account when predicting the actual potential of a power plant in dealing with an effective reinjection. One of the key parameters to assess is the solubility of the acid gas, as it influences the thermodynamic conditions (saturation pressure and temperature) of the fluid. Therefore, an enhanced solubility model for the CO_2-H_2S-water system is developed in this study, based on the mutual solubility of gases. The model covers a wide range of pressures and temperatures. The genetic algorithm is employed to calculate the correlation constants and corresponding solubility values of both CO_2 and H_2S as functions of pressure, temperature and the balance of the gas. The results are validated against previously published models and experimental data available in the literature. The proposed model estimates the pure gas solubility, which is also a feature of other models. The more innovative feature of the model is the solubility estimation of each CO_2 or H_2S in simultaneous presence, such as when the binary gas is injected into the pure water of the geothermal reinjection well. The proposed solubility model fits well with the available experimental data, with a mean deviation lower than 0.2%.

Keywords: solubility; geothermal fluids; NCG reinjection; acid gas

1. Introduction

Geothermal energy is generally recognised as a renewable resource, which is especially appealing because it is not hindered by the lack of constant resource availability, as is the case with solar, wind or wave energy. Compared to these, geothermal energy has a high power ratio (power over the covered surface area) and, due to the high drilling cost by a minimum of 2 M$/well [1], the power plant size typically ranges between 1 and 60 MWe.

Careful management of the geothermal field can guarantee a significant lifetime (>25 years with more than 7500 h/yr of operational time) for the geothermal energy conversion system; in the long-term, the issue of sustainability is primarily linked to the reservoir fluid balance. In the last decades, the fluid balance has improved significantly over the years with the extensive practice of condensate reinjection. The main issue, when shifted to the short-term and local scale, where relevant side effects are present, is the release of non-condensable gases (NCGs) to the environment. NCGs are commonly found in natural reservoirs and can contain several types of contaminants. The contaminants released by geothermal energy conversion systems (GECS) usually include H_2S, NH_3, CH_4, and, in some cases, Hg [2].

Geothermal power plants produce an average of about 120 g CO_2/kWh [3]. The CO_2 is found within the NCGs at high concentrations (exceeding 90%), and is typically released at the cooling

tower [4]; if routed back to the reservoir, it would not be released to the atmospheric environment, so that it should be at least classified as avoided emissions. One of the innovative solutions is the reinjection of NCGs into the reservoir, which has been investigated in recent years. The reinjection well is primarily used for the reinjection of water during power plant operation to improve resource recovery and wastewater disposal [5]. As shown in Figure 1, the NCGs and water can be reinjected into the reservoir through the same reinjection well by an annular pipe in which water and NCGs are flowing in the inner pipe and casing, respectively. Depending on the case study, the water-NCGs interaction can be simplified in the form of water-CO_2, water-H_2S or the water-CO_2-H_2S mixture. The full reinjection design is studied by Kaya et al. [6], who found that the reinjection of water-NCG mixture increases the reservoir pressure and enhances the early stages of production. Also, Fiaschi et al. reported that the content of NCGs remarkably affects the dynamic behavior of the reinjection process and should be precisely considered in the simulation of the reinjection well [7]. The gas is partially dissolved in the water and the remaining free gas is injected back into the reservoir by the static head of the liquid [5]. The saturated steam is extracted for energy generation and then it is recycled back to the reservoir [7]. The chemistry of geothermal fluid is one of the key design aspects of geothermal systems and the solubility of the gas in water is an important factor in the exploration, development, and use of geothermal resources. In order to effectively reinject the NCGs, which are mainly composed of CO_2 and H_2S, the properties of all fluids involved, and especially of the reinjection stream, need to be accurately assessed. The solubility is the most influential parameter for the reinjection as it directly affects the NCG-reinjection capacity, reinjection pressure, and saturation pressure/temperature [8].

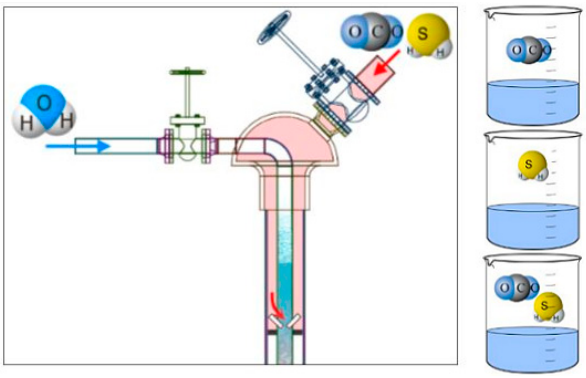


Figure 1. Schematic of the reinjection well and the process of non-condensable gas (NCG) injection into the downward flowing water.

Due to their wide practical application, the solubility of reactive gases like CO_2, H_2S has been a challenging topic for many years. As a result, recent studies have investigated the gas solubility in water or a water-based solvent. The studies include three categories: (1) determining the pure gas solubility in pure water, (2) focusing on the solubility of pure gas in a binary solvent, and (3) the solubility of pure gas in water containing additional dissolved constituents like free cations and anions. There are many empirical correlations for solubility estimation in all of these categories. However, there are few pieces of research about the solubility of the binary gas mixture in water. Savary et al. [9] performed an experimental investigation on CO_2-H_2S injection into pure water in a wide range of pressures and temperatures. This study has the most consistency with regards to the components and the thermodynamic condition with the NCG reinjection and, therefore, it is one of the main references of the current study. Shabani et al. [10] studied the gas mixture of CO_2-H_2S-CH_4-N_2 in brine by the non-iterative fugacity-activity thermodynamic model. Gu et al. [11] analysed the same model by an enthalpy-based model at high temperature and pressure conditions. Afsharpour [12,13] studied H_2S and CO_2-H_2S in aqueous solutions by the equation of state (EoS), which requires prediction of vapor-liquid equilibrium data and the thermal properties of pure and mixtures.

All of the mentioned studies performed a complete thermodynamic calculation using an appropriate equation of state and the related binary interaction coefficients. An alternative approach for finding the exact equilibrium concentrations in the gas-liquid mixture is direct correlations. The purpose of the present research is to derive a practical correlation for the solubility of binary CO_2-H_2S gas mixtures in water. The proposed correlation can be utilized not only in geothermal reinjection applications but also in other related processes such as biogas purification using water-scrubbers; this leads to saving computational time compared to frequently adopted EoS with phase equilibrium calculations. In addition, the method presented here is independent of the equation of state or external PVT database. This feature is essential for complicated models including the reinjection process [14]. The complexity of the model comes from the large computational domain and gird number in well modelling, and the solubility estimation is only a part of the overall one, therefore it is preferable to avoid involving complex EoS, as was done by Shafaei et al. (2012), who used a PVT program [15–17]. However, in order to overcome this bottleneck, it is necessary to introduce an appropriate solubility model for the modeling of geothermal applications, geological storage or underground aquifers. The current study introduces new correlations for the solubility modelling of pure CO_2, pure H_2S, and the CO_2-H_2S mixture in water at a wide range of pressures and temperatures, which meets the requirement of geothermal modelling. The pros and cons of different solubility models are listed in Table 1.

The physics of the injection is shown in Figure 2. There are two different types of interaction between phases. Interaction 1 is one-directional from the NCG-injection-feed into the water, while the other one is bidirectional for all components, including CO_2, H_2S and the water. All thermodynamic approaches are limited to type 2, which is based on the full equilibrium state, and both phases are allowed to receive and release any of the mixture components until the equilibrium is achieved and it is not recommended to use those ones with the composition of the NCGs as input. Thus, the main advantage of the proposed model compared to the thermodynamic ones is that it covers both types of interactions, especially the type 1, in which the fresh feed of NCG (with a fixed composition) is injected into the water by the driving force of pressure. Another advantage of the model compared to the previous correlations in the literature is that it is applicable not only for the pure gas injection, but also for the mixture of CO_2 and H_2S.

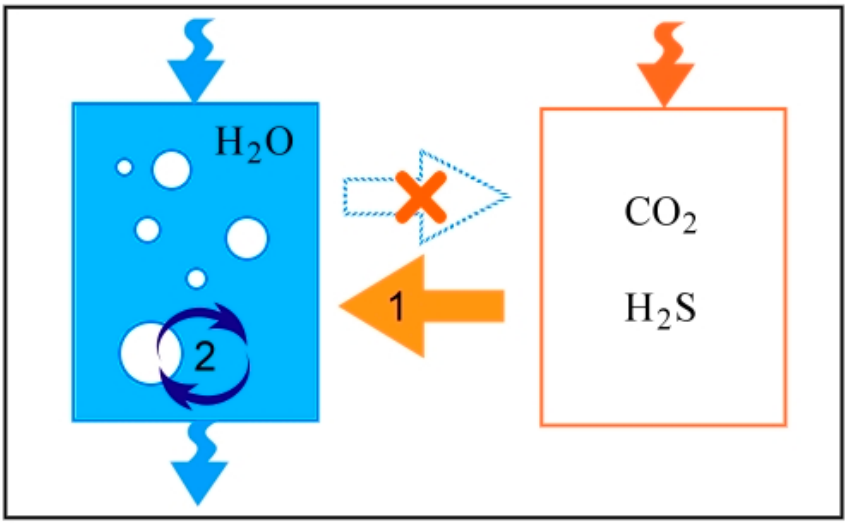


Figure 2. Phase interactions between gas and liquid in the reinjection point.

Table 1. Comparison of the solubility models subjected to the reinjection process in geothermal power plants.

Method	Approach	Advantages	Disadvantages	Application
Thermodynamic models	Two-phase equilibrium-state calculation	-High accuracy -Valid for a wide range of pressures and temperatures	-High computational cost -Dependency on the EoS -Partial inconsistency with the reinjection	All
PVT dataset [15–17]	Lookup-table properties	-Simple calculation by interpolation -Commercially used and already evaluated -Possibility of extrapolation	-Limited range of P, T or the composition -Partial inconsistency with the reinjection	Mainly available for oil and gas case studies
Literature correlations [18]	Deriving a formulation by using reference data	-Quick estimation -Ability to calculate the solubility in or out of the reference data -The accuracy of the model can be improved by adapting the form of the equation.	-Partial inconsistency with the reinjection -Limited to the solubility of pure gas in water or brine (e.g., CO_2 in water or H_2S in water)	Depends on the reference experimental data
Proposed correlation		-All of the advantages of the literature correlations -High reliability due to a large amount of reference data including both experimental and the thermodynamic-model data -Covering a wide range of P and T -Adapted to the physics of the injection process -Applicable for pure gas solubility -Applicable for mixture gas solubility and taking into account the interactions.	Limited to the solubility of CO_2-H_2S mixture in water	Reinjection of the CO_2-H_2S mixture in geothermal power plants.

In the present research, the final case study is defined according to the full reinjection scenario of the geothermal power plants located in the Larderello area of Italy. The resource conditions are characterized by a saturated vapour condition at a pressure within the 60–80 bar range, and 280 °C temperature at about 3500 m depth. At the wellhead, the expected resource conditions are 10.3 bar pressure and 180 °C temperature. The NCG mass content is estimated at about 8%, of which about 7.8% is CO_2 and 0.2% H_2S. The well layout consists of two production wells and one reinjection well. The heat is transferred to the binary-Organic Rankine Cycle (ORC) circuit, and the geothermal steam is condensed. The ORC is a recuperative power cycle using R1233zd(E) as working fluid. A three-stage compressor with intercoolers to reduce the power consumption was considered. The layout of the case study is displayed in Figure 3.

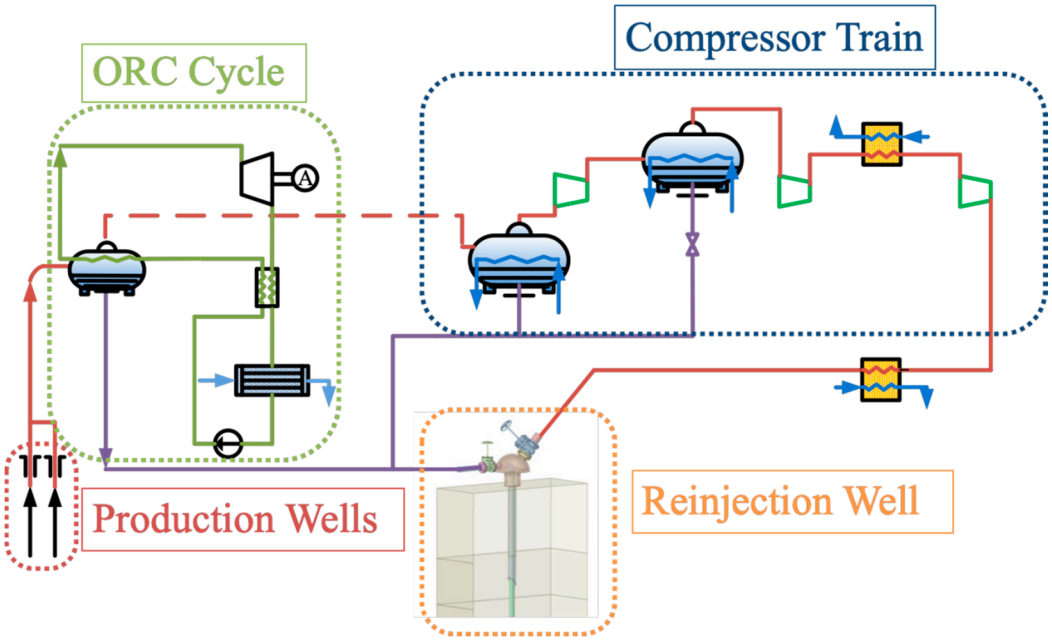


Figure 3. Schematic of the reinjection well and the process of NCG injection into the downward flowing water.

The challenge is that the NCG mass content of the steam is high (8%), which must be compressed and reinjected at a suitable depth in the reinjection well. The reinjection process design requires the precise computation of the mixture, therefore considering the solubility of NCGs (mainly CO_2) in the water. Moreover, the reinjection of CO_2 can be useful in the production of steam because the presence of CO_2 in the fluid preserves the pressure of the flash point of the fluid mixture, promotes boiling and enhances the enthalpy of the fluid produced by the reservoir. Therefore, all of the parameters, which may alter the CO_2 injection, should be precisely taken into account. One of them for the Larderello case study is the presence of H_2S in NCGs. The effect of the H_2S as a part of NCG is studied to see how much it can change the CO_2 solubility and the reinjection performance.

2. Methodology

The development of the model is based on the available experimental solubility data of pure CO_2, pure H_2S, the binary gas mixture in the pure water, and the results of commercial software. The type, the range, and the size of each set are listed in Table 2. Diamond et al. [18] collected the experimental CO_2 solubility data from several research studies from the year 1935 to 2002 [19–43].

Table 2. List of the reference data.

Type of Data	Reference	Pressure (MPa)	Temperature (°C)	Data N°
CO_2 in water	Diamond, 2003 [18]	0.1–100	0–100	520
H_2S in water	Lee, 1977 [44]	0–6.67	10–180	100
Binary gas (CO_2 + H_2S) in water	Savary, 2012 [9]	3.9–35	120 (fixed)	50
Binary gas (CO_2 + H_2S) in water	UniSim® [45]	0–15	0–150	190,000

The model is intended to provide an estimation of both pure H_2S and pure CO_2 solubility in water. In addition, it is adapted to estimate the solubility of the binary mixture of them in water. The proposed model for CO_2 and H_2S solubility in water (x: mole fraction) is defined according to Equations (1) and (2). The units of pressure (P) and temperature (T) within the correlation are MPa and °C.

$$x_{CO_2} = \left[\left(a_1T^2 + a_2T + a_3P^2 + a_4\right)^{a5} \times \frac{\ln(a_6\mathrm{P} + a_7)}{\mathrm{P}^{a_8}}\right] \times f\left(Y\prime_{CO_2}\right) \tag{1}$$

$$x_{H_2S} = \left[\left(b_1T^2 + b_2T + b_3P^2 + b_4\right)^{b5} \times \frac{\ln(b_6\mathrm{P} + b_7)}{\mathrm{P}^{b_8}}\right] \times g\left(Y\prime_{H_2S}\right) \tag{2}$$

The functions, f and g, are defined as

$$f\left(Y'_{CO_2}\right) = \left[a_9\left(Y\prime_{CO_2}\right)^{a_{10}} + a_{11}\left(Y\prime_{CO_2}\right)^{a_{12}} + a_{13}\left(Y\prime_{CO_2}\right)^{a_{14}}\right] / \left[a_9 + a_{11} + a_{13}\right] \tag{3}$$

$$g\left(Y'_{H_2S}\right) = \left[b_9\left(Y\prime_{H_2S}\right)^{b_{10}} + b_{11}\left(Y\prime_{H_2S}\right)^{b_{12}} + b_{13}\left(Y\prime_{H_2S}\right)^{b_{14}}\right] / \left[b_9 + b_{11} + b_{13}\right] \tag{4}$$

in which Y' is the relative mole fraction of each component in the gas phase (y), which is injected into the pure water:

$$Y'_{CO_2} = \frac{y_{CO_2}}{\left(y_{CO_2} + y_{H_2S}\right)} \tag{5}$$

$$Y\prime_{H_2S} = \frac{y_{H_2S}}{\left(y_{CO_2} + y_{H_2S}\right)} \tag{6}$$

The supporting idea for the above definition of the relative fraction is that it helps to make the model independent of the possible water vapor. For the pure gas solubility, the Y' is equal to one, and the equations are simplified into Equations (7) and (8):

$$x_{CO_2,pure} = \left(a_1T^2 + a_2T + a_3P^2 + a_4\right)^{a5} * \frac{\ln(a_6\mathrm{P} + a_7)}{\mathrm{P}^{a_8}} \tag{7}$$

$$x_{H_2S,\,pure} = \left(b_1T^2 + b_2T + b_3P^2 + b_4\right)^{b5} * \frac{\ln(b_6\mathrm{P} + b_7)}{\mathrm{P}^{b_8}} \tag{8}$$

The equations have nonlinear forms with coefficients of a_i for the solubility of CO_2 and b_i for the solubility of H_2S. Both Equations (1) and (2) consist of two parts, in analogy to the model of Duan et al. (2003), where the term responsible for the second dissolved components Equations (3) and (4) is multiplied by the part responsible for the solubility of the first component Equations (7) and (8) [19]. Duan et al. (2003) utilized a thermodynamic-based equation, which includes chemical potential and the fugacity coefficient; in their approach, both are correlated as functions of various combinations and permutations of pressure and temperature. In the present research, a deeper investigation and further analysis are conducted to improve the accuracy of the proposed model adapted for the binary gas injection. The model concept is shown in Figure 4, including a multi-objective optimization for computing the coefficients of the proposed correlations. The coefficients of a_i and b_i with index 1 to 8, correspond to Equations (7) and (8) or the main part of the Equations (1) and (2), and they are correlated by the retrieved experimental database for pure gas solubility. The remaining coefficients with indexes from 9 to 13 are correlated using the secondary (generated) database by UniSim®

software [45], which is a process simulation tool with a comprehensive library of thermodynamic models and an extensive property database. This software also includes a specific EoS for the sour gas applications. This study benefits from this thermodynamic solver for property estimation. The data covers a wide range of pressures and temperatures for different fractions of a binary gas mixture of H_2S and CO_2. The input variables for generating the secondary database are CO_2 fraction, H_2S fraction, temperature and pressure, while the outputs are the equilibrium stage fractions of all components. The validation of the UniSim® Sour Peng-Robinson (PR) model through the available experimental data is performed at this stage (construction of secondary database).

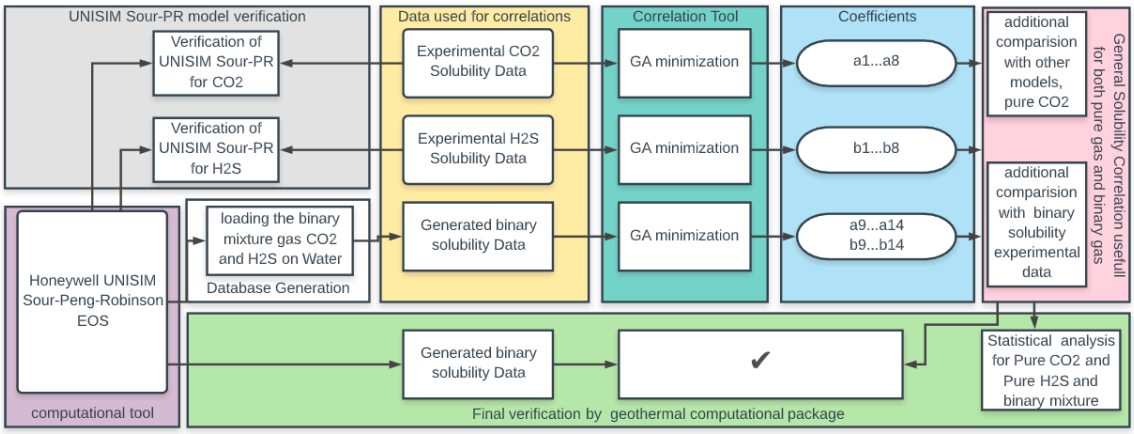


Figure 4. Process diagram of the research.

The coefficients are correlated at three stages, in which independent error minimization procedures are applied following the form of Equation (9), where $x_{i,j}$ is the calculated value and $\acute{x}_{i,j}$ is the experimental or the reference value. Two optimization steps are involved, one for the pure gas solubility (Equations (7) and (8)) and another one concerns the solubility of the gas mixture (Equations (1) and (2)). The genetic algorithm (GA) is a heuristic search approach based on natural selection which is a reliable method for complex optimization case studies [46]. This method works effectively for the proposed nonlinear correlations with thirteen coefficients each. The termination condition for the random search is considered, searching the minimum of the following objective function:

$$Min \ : \ \sum_{j=1}^{m} \sum_{i}^{n} \left(\left(x_{i,j} - \acute{x}_{i,j} \right)^2 \right) \tag{9}$$

The proposed minimization method has no limits for the form of correlation of equations and the number of coefficients. The convergence of the optimization procedures is obtained within the limit of 10,000 iterations.

3. Results and Discussion

The multivariable regression described in the previous section is developed in MATLAB. The inputs of the minimization by GA are the reference data and the outputs are the coefficients of Equations (1) and (2), which are listed in Table 3 for both CO_2 and H_2S.

Table 3. Calculated coefficients of the proposed model.

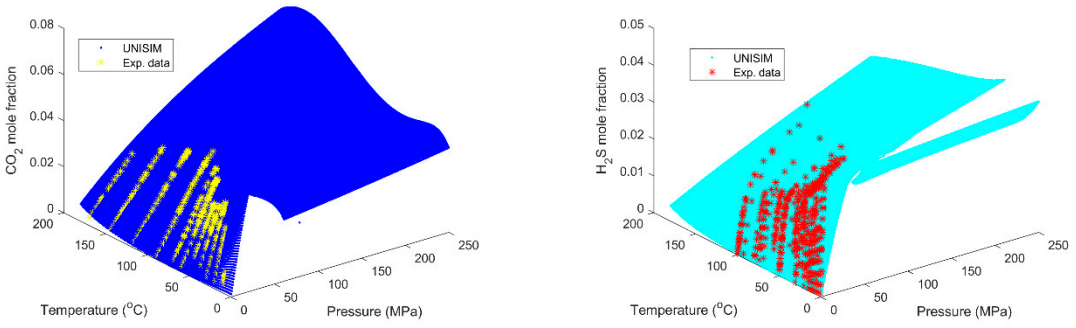
Index	Coefficients for CO_2 (a_i)	Coefficients for H_2S (b_i)
1	5.1392×10^{-1}	2.4812×10^{-1}
2	$4.7999 \times 10^{+1}$	8.0370
3	$3.0091 \times 10^{+1}$	$7.3159 \times 10^{+1}$
4	$6.3701 \times 10^{+2}$	$8.7230 \times 10^{+1}$
5	-6.7389×10^{-1}	-6.1670×10^{-1}
6	1.0548×10^{-1}	1.9911×10^{-1}
7	2.6740	2.0354
8	-7.9216×10^{-1}	−1.0341
9	5.9794	4.1092
10	7.0812×10^{-1}	7.4443×10^{-1}
11	$2.1386 \times 10^{+1}$	$2.4380 \times 10^{+1}$
12	7.1616×10^{-1}	$1.2383 \times 10^{+2}$
13	$5.4354 \times 10^{+1}$	$1.7089 \times 10^{+1}$
14	7.0093×10^{-1}	7.4445×10^{-1}

If $Y\prime_{CO_2} = 1$, then x_{CO_2} would be the solubility of the pure CO_2 as a function of pressure and temperature. The same concept is valid for H_2S. The statistical analysis is performed for the correlations, with results shown in Table 4, demonstrating that the solubility of pure CO_2, pure H_2S, and of binary CO_2-H_2S gas mixtures can be estimated by the proposed model with reasonable accuracy.

Table 4. Statistical analysis of the correlations.

Case	R^2	*MSE*	*MAE*
CO_2 in water	0.9803	6.11×10^{-6}	1.067×10^{-3}
H_2S in water	0.9833	2.10×10^{-6}	5.331×10^{-4}
Partial solubility of CO_2 in water	0.9529	2.90×10^{-5}	1.326×10^{-3}
Partial solubility of H_2S in water	0.9733	7.79×10^{-4}	5.226×10^{-3}

The results of the Sour-PR model, derived by the UniSim® package and supplemented by the experimental data, are depicted in Figure 5 for pure gases; this agreement confirms that the UniSim model is eligible for generating a secondary database of binary solubility data. The secondary database is used for correlating the partial solubility of CO_2 and H_2S.



(**a**) (**b**)

Figure 5. Evaluation of the UniSim® results for pure CO_2 (**a**) and H_2S (**b**) solubility.

The solubility of pure CO_2 is estimated by the model and compared with the experimental data (Figure 6a); the results of Duan et al. (2003), which are regarded as one of the most accepted for CO_2 solubility in water, are illustrated in Figure 6b [47].

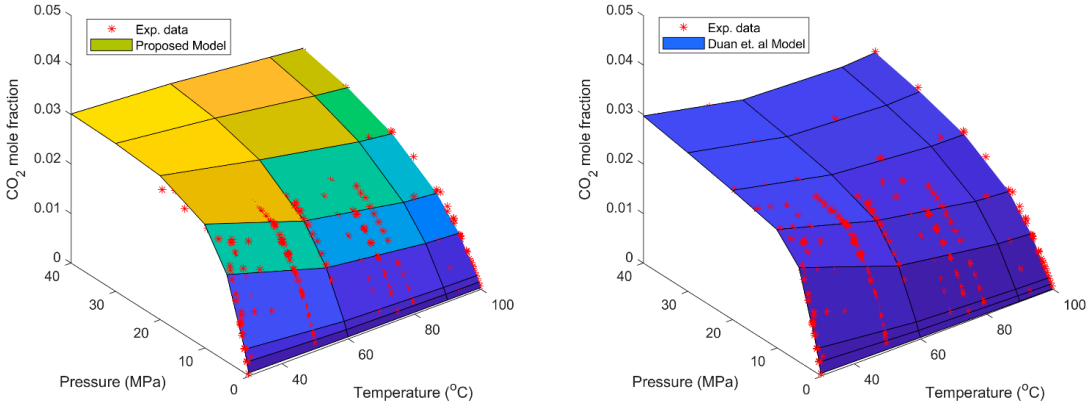


Figure 6. Evaluation of pure CO_2 solubility with experimental data and other models ((**a**): Duan et al. (2003) and experimental data (Diamond et al. 2003); (**b**): proposed model and experimental data (Diamond et al. 2003)).

The results of the proposed model for H_2S solubility in water are compared with the experimental data of Lee et al., as is shown in Figure 7.

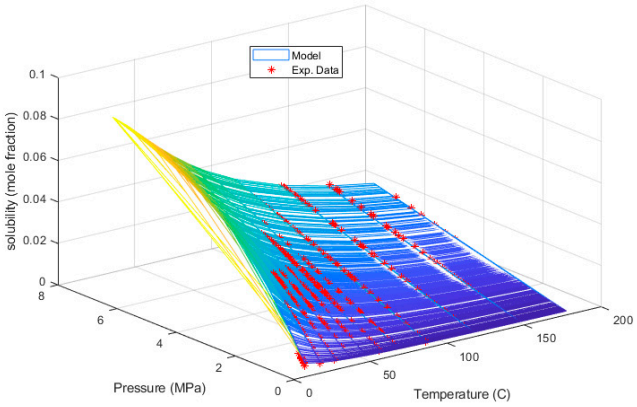


Figure 7. Validation of pure H_2S solubility with experimental data (Diamond et al. research).

Due to the availability of a large number of experimental data for CO_2 solubility in water, an additional assessment for model reliability is performed by comparing the model prediction with some literature data out of the reference database. The selected researches on CO_2 solubility are from Valtz et al. [48], Gu. et al. [49] and Tang et al. [50], representing the low-temperature condition, and Chapoy et al. [51], Hou et al. [52], and Pfohl et al. [53], belonging to the high-temperature range. These data were used neither in the previous steps of the dataset generation nor in the optimization process. As shown in Figure 8, there is a good agreement between our model and the published experimental data (number of data: 28), and the R^2 value of 95.4% shows how well the proposed model fits the reference data.

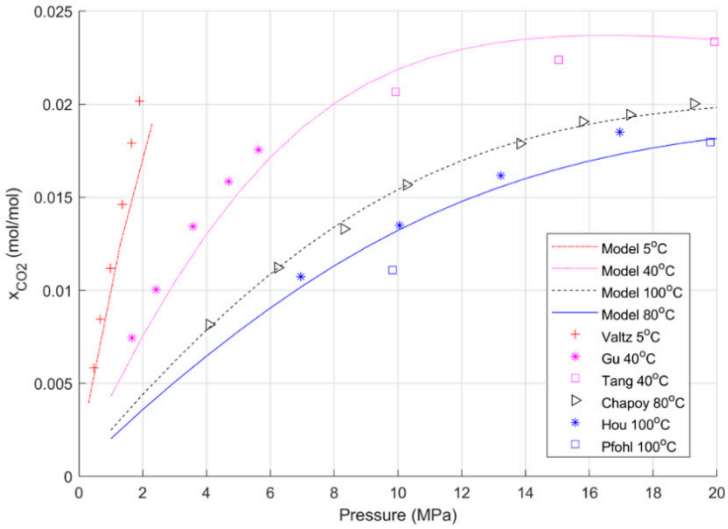
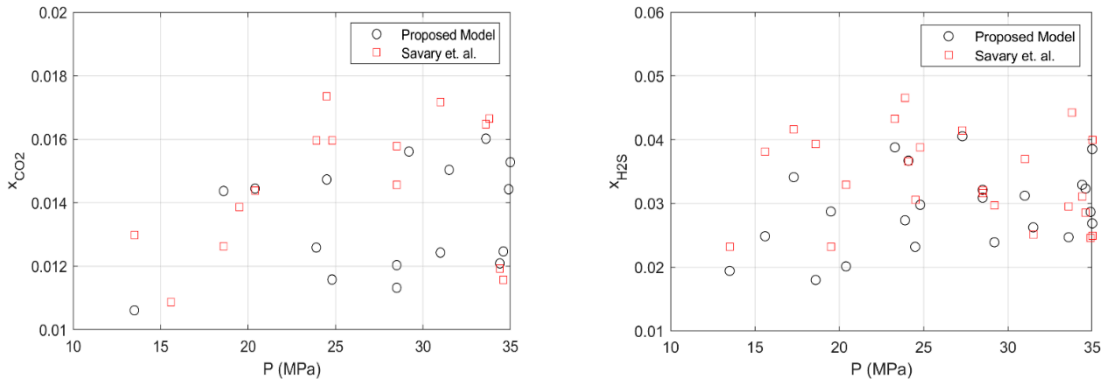


Figure 8. Validation of pure H_2S solubility with new experimental data. (No intersection with Diamond et al. research).

As previously discussed, the coefficients of a_9 to a_{14} and b_9 to b_{14} in Equations (3) and (4) are derived from a secondary database, previously validated by experimental data. In order to evaluate the binary gas solubility, the results of the proposed model are directly compared with available experimental data (Savary et al. [9]). As shown in Figure 9, the model results reveal a satisfactory agreement with experimental data, with an absolute deviation of 0.3% for the mixture solubility.



(**a**) (**b**)

Figure 9. Validation of mixture solubility model 120 °C for CO_2 (**a**) and H_2S (**b**).

In the last part, the model reveals the impact of H_2S on the solubility of CO_2 as the dominant component of NCGs. In order to evaluate the extent of this effect, a case study of the total reinjection binary geothermal pilot power plant designed for the Larderello area in Italy is considered. In this case study, the NCG stream composition accounts for about 3% of H_2S and 97% of CO_2, and the stream is reinjected into the reservoir water. Although the mentioned amount of H_2S is very low, it decreases the capacity of water to dissolve the CO_2. As shown in Figure 10, the actual solubility of CO_2 for the reinjection well (high pressure) is up to 0.05% lower than in the case where H_2S is not present. Thus, neglecting the effect of H_2S causes a significant deviation from the actual amount of dissolved CO_2. However, the proposed model incorporates both the effect of H_2S on the solubility of CO_2 and vice versa.

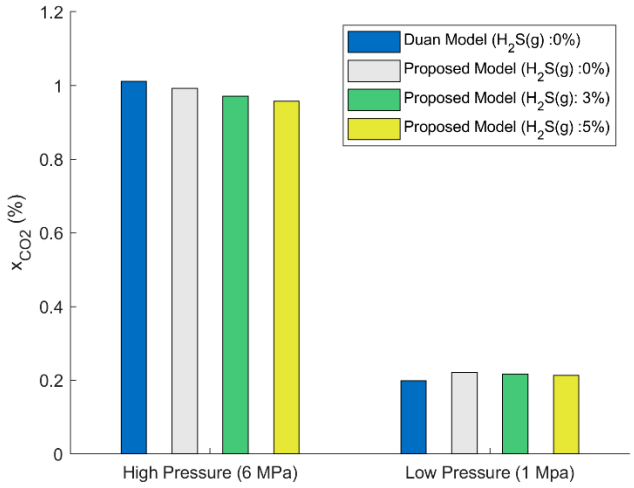


Figure 10. Geothermal case study: effect of H_2S on the solubility of CO_2 (Temperature: 89 °C).

To better understand how this deviation in the estimation of solubility may influence the design, the relative solubility error (e_r) is calculated according to Equation (10):

$$e_r = (x_{Duan_model} - x_{proposed_model}) / x_{proposed_model} \quad (10)$$

In an assumed scenario, where all NCGs are expected to be dissolved into the water, previous models which neglect the H_2S effect (including the Duan et al. Model) calculate the relative solubility error as 4% and 5.6% for NCGs with 3% and 5% of H_2S, respectively. The vertical depth of the NCG injection valve depends on both the static head of the water and the solubility of CO_2 at injection point, which is roughly calculated according to Equation (11):

$$Depth_{valve} = P / (\rho_{water} \times g) \quad (11)$$

In which, ρ is the density and g is the gravity acceleration. Also, the pressure is calculated according to Equation (1) using a known value of solubility. Thus, in the reinjection well design by previous solubility models, an error of about +50 m is induced in the location of the valves, which may cause process failure.

4. Conclusions

The objective of the present study is the development of a model suitable for geothermal applications facing gas mixture solubility, where in most cases the gas is not pure. As one of the most common ones, the binary mixture of CO_2-H_2S is studied, which is primarily applicable in the reinjection process. The experimental data are collected from the literature, including 670 data (Table 2) covering a wide range of pressures and temperatures, belonging to pure CO_2, pure H_2S and the mixture. In order to overcome the limited number of data for binary mixture [9], a thermodynamic-based-model consisting of 190,000 data is generated and then validated with all of the available experimental data. The proposed model is developed by a genetic algorithm, based on both the experimental and the artificial datasets. The model is able to estimate the solubility of pure CO_2 and pure H_2S, as well as their binary mixture, in water. The coefficient of determination (R^2) of the model is 0.98 for the pure gas and between 0.95 and 0.98 for the mixture, which appears to be a good quality for correlation derivation. Furthermore, the predictions made by the proposed model are validated by comparing them with some recent literature data, and the average of mean absolute deviation values for pure H_2S, pure CO_2 is calculated as 0.2%. Besides, the decrease of the CO_2 solubility due to the presence of H_2S is reported as up to 4% for the geothermal case study. The present model precisely considers the effect

of the second NCG component and prevents the overestimation of gas solubility in water, which is essential for the NCG reinjection capacity and the design of the surface equipment.

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