Simulations of the Impact of Co-injected Gases on CO 2 Storage, the SIGARRR Project: Processes and Geochemical Approaches for Gas-water-Salt Interactions Modeling

Jérôme Corvisier, Martha Hajiw, Elise El Ahmar, Christophe Coquelet, Jérôme Sterpenich, Romain Privat, Jean-Noël Jaubert, Karine Ballerat-Busserolles, Jean-Yves Coxam, Pierre Cézac, et al.

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Simulations of the impact of co-injected gases on CO_2 storage, the SIGARRR project: processes and geochemical approaches for gas-water-salt interactions modeling

Jerome Corvisier[a,*], Martha Hajiw[b], Elise El Ahmar[b], Christophe Coquelet[b], Jérôme Sterpenich[c], Romain Privat[d], Jean-Noël Jaubert[d], Karine Ballerat-Busserolles[e], Jean-Yves Coxam[e], Pierre Cézac[f], François Contamine[f], Jean-Paul Serin[f], Véronique Lachet[g], Benoit Creton[g], Marc Parmentier[h], Joachim Tremosa[h], Philippe Blanc[h], Laurent André[h], Louis de Lary[h], Eric C. Gaucher[i]

[a]*MINES ParisTech, PSL Research University, Centre de Géosciences, 35 rue Saint-Honoré 77305 Fontainebleau – France*
[b]*MINES ParisTech, PSL Research University, Centre Thermodynamique des Procédés, 35 rue Saint-Honoré 77305 Fontainebleau – France*
[c]*Université de Lorraine, GéoRessources UMR CNRS 7359, BP 70239 Faculté des Sciences et Technologie 54506 Vandoeuvre-lès-Nancy – France*
[d]*Université de Lorraine, LRGP-ENSIC UMR CNRS 7274, BP 20451 1 rue Granville 54001 Nancy – France*
[e]*Université Blaise Pascal Clermont-Ferrand 2, ICCF UMR CNRS/UBP 6296, 24 avenue des Landais 63177 Aubière – France*
[f]*Université de Pau et des Pays de l'Adour, ENSGTI LaTEP EA 1932, BP 7511 rue Jules Ferry 64075 Pau –France*
[g]*IFP Energies Nouvelles, 1 et 4 avenue de Bois-PRéau 92852 Rueil-Malmaison – France*
[h]*BRGM, 3 avenue Claude Guillemin BP 36009 45060 Orléans cedex 2 – France*
[i]*TOTAL, CSTJF, avenue Larribau F-64018 Pau – France*

Abstract

The composition of the captured CO_2 mixture may considerably vary both qualitatively and quantitatively depending on the sources, the selected technologies for purification... Many other compounds could be co-captured at various concentration levels and their potential co-storage along with CO_2 could be considered. Since these compounds may change the behavior of the CO_2 rich mixture, operators of the whole CCTS chain therefore wait for

* Corresponding author. Tel.: +3-316-469-4750; fax: +3-316-469-4713.
 E-mail address: jerome.corvisier@mines-paristech.fr

clear recommendations in terms of admissible concentration levels for the various co-injected impurities while regulators need tools allowing them to formulate these recommendations. The SIGARRR project aims at conducting precise geochemical simulations to model the long-term behavior of co-injected gases within CO_2 storage sites based on a combination of experimental and numerical approaches, to ensure the reliability of numerical simulations. Within this context and the recent improvements in both processes and geochemical codes, this paper presents the water solubility precise calculations for CO_2 and most of the potential impurities N_2, O_2, Ar, CO, H_2S, SO_2, CH_4, H_2 and the brine solubility relatively accurate geochemical simulations for CO_2, N_2, O_2 and CH_4 as well.

1. Introduction

An important part of the induced cost of Carbon Capture, Transport and Storage (CCTS) comes from the separation step when CO_2 is separated from other gaseous compounds. The composition of the captured gaseous mixture may considerably vary both qualitatively and quantitatively depending on the sources, the selected technologies for purification... Many other compounds could be co-captured at various concentration levels [1] and their potential co-storage along with CO_2 is considered. If acceptable, an increase of the impurities concentrations can significantly reduce capture costs and consequently contributes to a faster deployment of CCTS technologies. Nevertheless, some of these impurities could be toxic regarding environment or even human health and/or could chemically react with water, mineral phases or materials involved on storage sites. These compounds and their induced reactions may change the behavior of the CO_2 rich mixture [2], may affect the permeability of the cap rock and then potentially contaminate surrounding environments.

Operators of the whole CCTS chain therefore wait for clear recommendations in terms of admissible concentration levels for the various co-injected impurities while regulators need tools allowing them to formulate these recommendations. Testing scenarios with accurate reactive-transport codes, validated and calibrated regarding laboratory experiments, should enable to propose these awaited precise recommendations.

The main thrust of purpose of the SIGARRR project, funded by the ANR, started in late 2013, is to be able to conduct precise geochemical simulations to model the long-term behavior of co-injected gases within CO_2 storage sites focusing on the:

- Impact of CO_2 and co-injected gases (SO_2, NO, O_2) on the minerals and reservoir (silicates + clay minerals) geochemistry,
- Possible inferences on the environment in case of leak.

The SIGARRR project proposes thus to combine experimental and numerical approaches, to ensure the reliability of numerical simulations. A part of the project consists naturally in experimental (using various technical approaches, e.g. [3]) or pseudo-experimental (*i.e.* molecular simulation, e.g. [4]) acquisition of thermodynamic data (vapor-liquid equilibrium properties) for CO_2 rich systems with increasing complexity: gas mixtures, gas mixtures+water, gas mixtures+brine and gas mixtures+brine+rock. Adapted Equations of State (EoS) were also developed and parameterized on relevant data [4-7]. Within the frame of the SIGARRR project, recent improvements in geochemical codes, such as CHESS developed by MINES ParisTech, allow to deal with non-ideal gas mixtures and to reproduce rather accurately existing solubility measurements for CO_2, other gases and even mixtures [8,9].

This paper aims at summing up the geochemical approach, both the parameters collected from the literature and some fitted parameters, and at comparing its capability to predict both the measured solubility of gases in pure water and co-solubility of water in the gas phase with other processes approaches developed within the project (E-PPR78 for Predictive Peng-Robinson, e.g. [4-6] and GC-PR-CPA for Cubic Plus Association using Peng-Robinson EOS and the Group Contribution method [7]). The ability of modeling of gas solubility in simple salt solutions and complex brine using recent datasets will also be demonstrated.

Nomenclature

R	perfect gas constant
T	temperature
P	pressure
V	molar volume
P^{sat}	saturated vapor pressure
f	fugacity
x, y	molar fractions in the liquid or gas phase respectively
m	aqueous molality
H	Henry's law constant
v^{∞}	molar volume of the component i at infinite dilution
γ	aqueous activity coefficient
ϕ	fugacity coefficient
T_c	critical pressure
P_c	critical pressure
ω	acentric factor
a	Peng-Robinson first parameter
b	Peng-Robinson second parameter
k_{ij}	binary interaction parameter in the gaseous phase for the Peng-Robinson EOS
ε_{ij}	binary interaction parameter in the aqueous phase for the SIT model

2. Water-gas equilibrium modeling

When considering a system of known temperature, pressure and composition, its equilibrium could be monophasic or multiphasic but its Gibbs energy should be minimal. To avoid minimization calculations, equilibrium conditions could also be determined admitting that they are equal in each phase, even though this condition is not sufficient and should be coupled to a stability criterion. This leads to the following relation between fugacities in both liquid and gas phase for each component:

$$f_i^l(T,P,x) = f_i^g(T,P,y). \tag{1}$$

In geochemistry, the asymmetrical approach consists in calculating activity coefficients in the liquid phase and an Equation of State for the gas phase. This method conducts to reformulate the equation (1) as Henry's law *i.e.* a function of activity, fugacity coefficient and molar fractions:

$$\gamma_i x_i H_i(T,P) = \phi_i^g y_i P \tag{2}$$

With H_i, the Henry's law constant that could be detailed:

$$H_i(T,P) = H_i(T,P^{sat}) exp \left(\frac{v_i^{\infty}(P-P^{sat})}{RT} \right) \tag{3}$$

Using v_i^{∞}, the molar volume of the component i at infinite dilution.

In processes, a symmetrical approach, where the same model is chosen to represent both liquid and gas phases, is more conventional, particularly for high pressures. Following this scheme the equation (1) is then rewritten:

$$\phi_i^l(T,P,x_i)x_i = \phi_i^g(T,P,y_i)y_i \tag{4}$$

In both cases, an equation of state is needed to calculate the fugacity coefficients. The EOS should also be adapted to multi-components as well as the selected mixing rules used to compute its parameters.

2.1. Peng-Robinson (PR) equation of state

The cubic Peng-Robinson equation of state [10] is one of the most widespread EOS and has already been implemented in the geochemical code CHESS [8,9] and is written as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{5}$$

Using a(T) and b, Peng-Robinson parameters defined by:

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T, T_c, \omega) \tag{6}$$

$$\alpha(T, T_c, \omega) = \left(1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2 \tag{7}$$

$$b = 0.07780 \frac{RT_c}{P_c} \tag{8}$$

The classical mixing rule shall also be considered:

$$a^{mix} = \sum_i \sum_j y_i y_j \left(1 - k_{ij}\right) \sqrt{a_i} \sqrt{a_j} \tag{9}$$

$$b^{mix} = \sum_i y_i b_i \tag{10}$$

with k_{ij} being binary interaction parameters between the compounds i and j.

In this case the fugacity of the ith compound is written as follows:

$$ln\,\phi_i = \frac{b_i}{b^{mix}}\left(\frac{PV}{RT} - 1\right) - ln\left(\frac{PV - Pb^{mix}}{RT}\right) - \frac{a^{mix}}{2\sqrt{2}RTb^{mix}} ln\left(\frac{V + 2.414b^{mix}}{V - 0.414b^{mix}}\right)\left(\frac{2\sum_j y_i(1 - k_{ij})\sqrt{a_i}\sqrt{a_j}}{a^{mix}} - \frac{b_i}{b^{mix}}\right) \tag{11}$$

2.2. Specific Ion Theory (SIT) aqueous activity model

Concerning the electrolytic part, very important for gas-water-salt systems, various models are available to compute the aqueous activity coefficients. Simple models based on long-distance electrostatic interaction are valid for diluted solutions only (i.e. Debye-Hückel, Davies, b-dot). Above a limit around 3M, for highly saline solutions, non-electrostatic short distance interactions could not be neglected. The Specific Ion-Interaction Theory (SIT) model [11,12], implemented in CHESS, allow to obtain good results for these solutions. The SIT approach, first mentioned by Bronsted [11], takes into account the short-distance forces by adding terms to the classical Debye-Hückel law. Theoretical details of the approach are given in Grenthe's work [12]. For neutral species like dissolved gas, only the "SIT" terms are of interest, and the SIT model limits to:

$$log\,\gamma_i = \sum_j m_j \varepsilon_{ij} \tag{12}$$

This approach can be compared to a Pitzer model where the third order interactions would be neglected and hence converting Pitzer parameters into SIT parameters is very convenient to fill some blanks in databases.

3. Parameters from the literature for geochemical modeling

From the previous sections, necessary models and subsequent parameters for a good representation of water-gas interactions in geochemical codes were highlighted and can be recalled up at this point.

3.1. Specific parameters for pure gases

Critical properties and acentric factors are the first parameters needed for water-gas interactions modeling. They can be retrieved from many sources and all are in rather good agreement. The retained values are from Yaws' Handbook [13] and are presented in Tab.1.

Table 1. Sources for Henry's law constants. Values for critical temperature and pressure and acentric factors. Fitted molar volume at infinite dilution and gas-water binary interaction parameters.

Compound	$H_i(T, P^{sat})$ Reference	T_c [K]	P_c [bar]	Acentric factor	v_i^{∞} [cm^3.mol^{-1}]	k_{i,H_2O}
CO_2	[14]	304.19 [13]	73.82 [13]	0.228 [13]	27.6, *this study*	0.198, *this study*
N_2	[15]	126.10 [13]	33.94 [13]	0.040 [13]	30.4, *this study*	0.455, *this study*
O_2	[16]	154.58 [13]	50.43 [13]	0.022 [13]	17.4, *this study*	0.621, *this study*
Ar	[15]	150.86 [13]	48.98 [13]	0.000 [13]	25.6, *this study*	0.590, *this study*
CO	[15]	132.92 [13]	34.99 [13]	0.066 [13]	15.2, *this study*	0.266, *this study*
SO_2	[17]	430.75 [13]	78.84 [13]	0.245 [13]	665.0, *this study*	-
H_2S	[18]	373.53 [13]	89.63 [13]	0.083 [13]	-77.8, *this study*	0.151, *this study*
CH_4	[19]	190.58 [13]	46.04 [13]	0.011 [13]	36.3, *this study*	0.507, *this study*
H_2	[17]	33.18 [13]	13.13 [13]	-0.220 [13]	14.9, *this study*	0.529, *this study*

3.2. Specific parameters for gas solubilities in water

Most important parameters in such models are probably Henry's law constants since they fix solubilities for gases. Quite a lot of references can be found depending on the considered gases: experimental values and models of various forms. Different models were then tested and only the retained ones are used in this study and presented in Tab. 1.

Concerning molar volumes, they can be obtained from the revised HKF general equation (Helgeson-Kirkham-Flowers, not detailed here) and the associated parameters for this equation can be obtained from various sources of the literature. Nevertheless, this parameter important for the pressure dependence of the Henry's law constant could be used as a fitting parameter, the only one for the gas solubility calculation. The optimized values as well as the number of experimental data used for fitting are presented in Tab. 1.

3.3. Specific parameters for gas solubilities in saline aqueous solutions

SIT binary interactions parameters can also be found in various studies such as parameters fitted on experimental data. In this study, parameters are collected from Millero [20 and references therein].

3.4. Specific parameters for gas mixtures

Binary interactions parameters for gas-water interactions can also be found in the literature but are also used as a fitting parameter, for the water-content calculation this time. Optimized values and the number of experimental data used for fitting are also presented in Tab. 1. The other binary interactions parameters are obtained for experimental data on binary equilibriums and they depend on both the chosen EOS and the associated mixing rule. They are generally independent regarding temperature. Here again, some existing modeling studies present most of the needed parameters [21-22].

All CHESS simulations presented here are run using the LLNL database (V8.R6).

4. Simulations of binary pure gas+water systems

4.1. CO_2

First, our model's ability to represent CO_2 solubility in water was tested since an important amount of reliable data is available in the literature. As shown on Fig. 1, the model, combined with the right selection of parameters (see Table 1.), represents very well the laboratory measurements, both the CO_2 solubility into water and the water content in the gas phase.
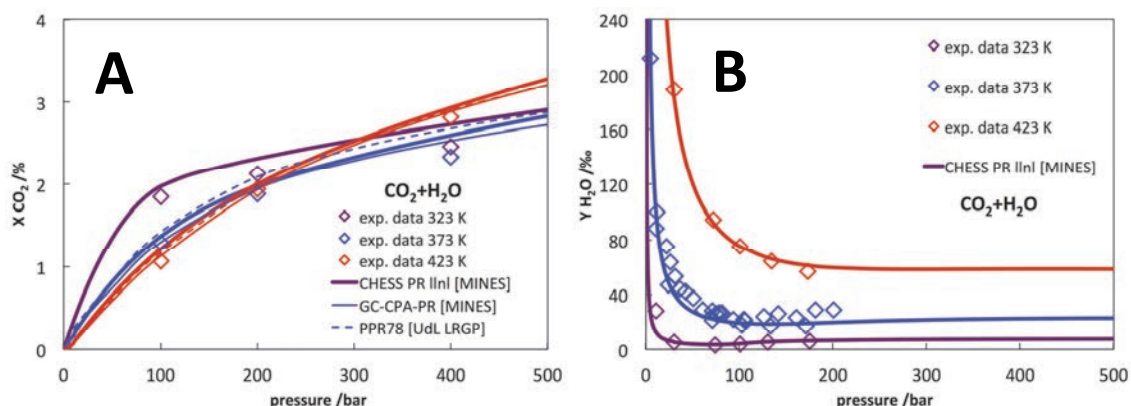

Fig. 1. Aqueous molar fraction (A) CO_2 and (B) H_2O vs. pressure for CO_2+H_2O system at various temperatures. Symbols correspond to experimental measurements [3,23,24], thin solid lines to GC-PR-CPA model, thin dotted lines to E-PPR78 model and bold solid lines to CHESS simulations.

On the same figure (Fig. 1A), the predictions of two symmetrical approaches GC-PR-CPA (Cubic Plus Association using Peng-Robinson EOS and the Group Contribution method [7]) and E-PPR78 (for Predictive Peng-Robinson, e.g. [4-6]) are also represented. These three models are in rather good agreement with the chosen experimental data.

4.2. Other gases

Models predictions can be compared over all experimental data found in the literature and over the whole range of temperature and pressure for each binary system. The Absolute Average Deviation (AAD) in percent is then calculated:

$$AAD = \frac{100}{N} \sum_{i=1}^{N} \frac{\left| x_i^{exp} - x_i^{model} \right|}{x_i^{exp}}. \tag{13}$$

Calculated deviations are presented in Tab. 2. In general, predictions with the geochemical are in good agreement with experimental data (both solubility and water content). GC-PR-CPA shows more deviations for carbon dioxide. E-PPR78 EoS predicts correctly solubility data, except for nitrogen and hydrogen. CHESS seems rather good except for SO_2, which is probably due to experimental measurements discrepancy and some of our asumptions.

Table 2. Deviations between experimental data and predictions with SIGARRR three models.

	Number of exp. data		GC-PR-CPA		E-PPR78		CHESS	
	x	y H_2O	x AAD [%]	y H_2O AAD [%]	x AAD [%]	y H_2O AAD [%]	x AAD [%]	y H_2O AAD [%]
CO_2	1803	426	8.2	29.3	6.3	14.2	5.5	9.0
N_2	561	163	3.7	9.8	84.0	4.7	3.6	5.3
O_2	835	14	4.1	13.0	71.4	69.2	4.0	0.6
Ar	298	28	2.3	8.9	-	-	2.8	1.3
CO	193	17	6.2	1.9	-	-	9.3	3.0
SO_2	393	-	16.0	-	13.2	-	15.6	-
H_2S	704	183	6.0	11.6	3.4	8.1	7.9	7.2
CH_4	719	319	7.0	16.2	10.2	6.5	6.7	6.2
H_2	571	17	7.4	5.4	>100	21.4	3.8	3.3

The predictions of CHESS model versus pressure are also presented on Fig. 2 for each gas-water systems along with a selection of experimental data.

The fitted values for molar volumes at infinite dilution correspond more or less to measured values from the literature, except for SO_2 and H_2S. In our model, a single constant value is used for each compound and this value is fitted to obtain the best AAD for all data over the whole pressure/temperature domain. The high fitted value for SO_2 and the low fitted value for H_2S are mainly due to their different behaviors regarding other compounds and their very high solubilities.
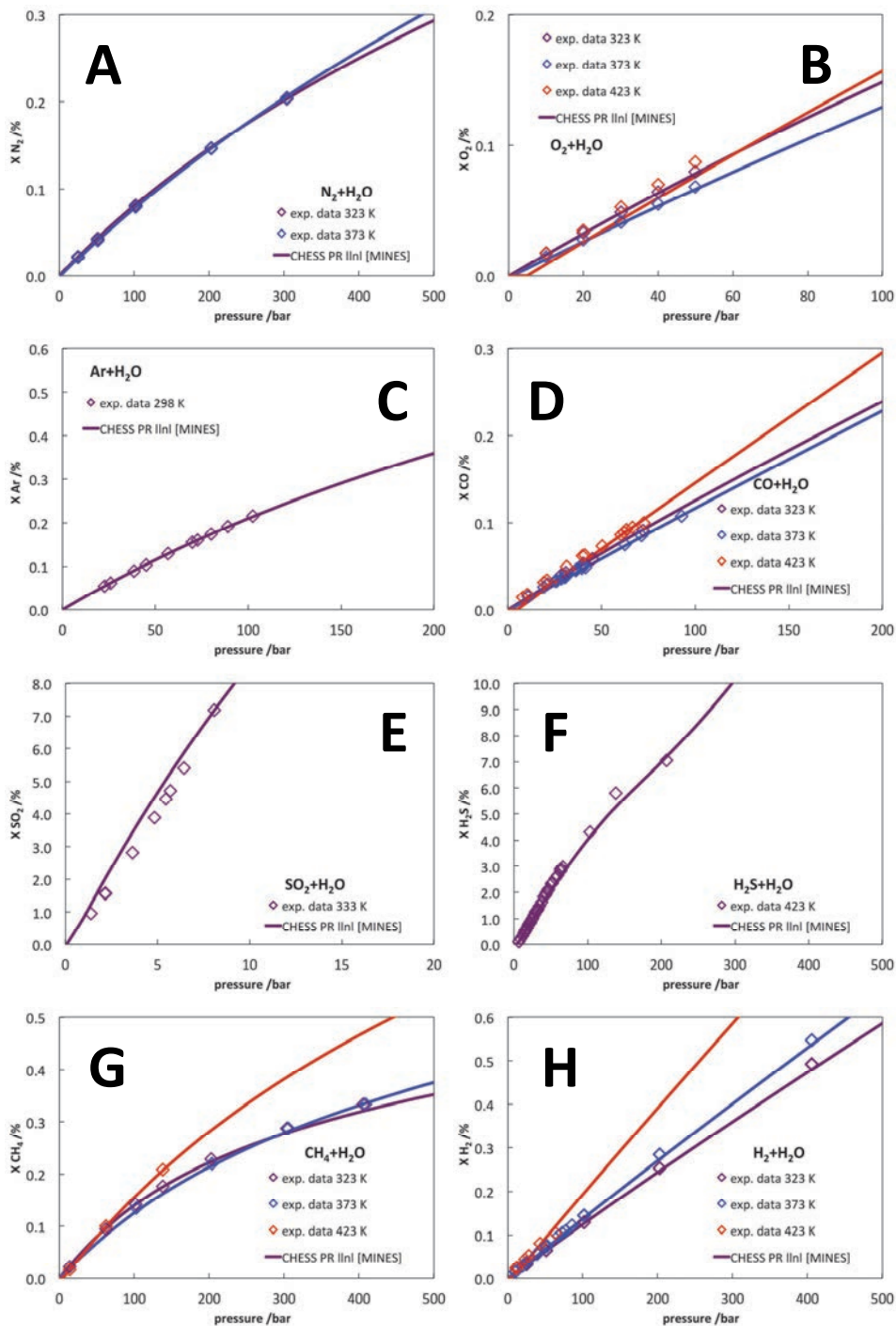
Fig. 2. Aqueous molar fraction (A) N_2, (B) O_2, (C) Ar, (D) CO, (E) SO_2, (F) H_2S, (G) CH_4 and (H) H_2 vs. pressure for various gas+water systems and various temperatures. Symbols correspond to experimental measurements from the literature [25-33] and bold solid lines to CHESS simulations.

5. Simulations of ternary gas mixtures+water systems

In our previous study [9], geochemical simulations of CO_2+N_2 and CO_2+CH_4 systems were successfully compared to literature data. Here, as a validation of our three models, their ability to model new experimental data on two CO_2+O_2 and CO_2+SO_2 other systems (acquired within the SIGARRR project using the method described in a previous publication [34], but not published yet) are tested.

5.1. CO_2+SO_2

The three models were used to simulate a 95% CO_2 and 5% SO_2 gas mixture in contact with water at 353 K and pressures up to 300 bar and the obtained results were plotted along with new experimental data on Fig. 3. All the models represent both the CO_2 and SO_2 dissolved molar fraction reasonably well.
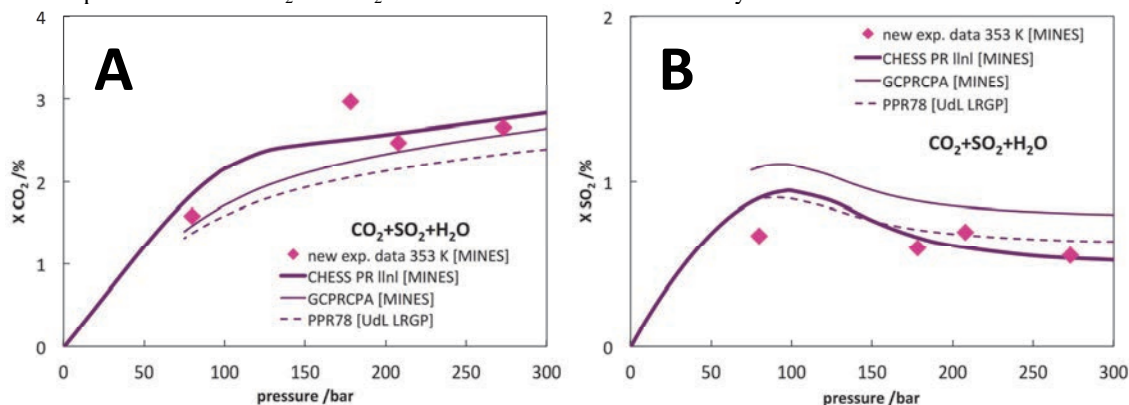

Fig. 3. Aqueous molar fraction (A) CO_2 and (B) SO_2 vs. pressure for CO_2-SO_2-H_2O system (95%. CO_2 and 5%. SO_2) at 353 K. Symbols correspond to new measurements, thin solid lines to GC-PR-CPA model, thin dotted lines to PPR78 model and bold solid lines to CHESS simulations.

5.2. CO_2+O_2

A 50% CO_2 and 50% O_2 gas mixture in contact with water at 353 K and pressures up to 300 bar was also simulated and the obtained results were plotted along with new experimental data on Fig. 4. All the models represent both the CO_2 and O_2 dissolved molar fraction relatively well, with a small overestimation of the dissolved oxygen at pressures greater than 100 bar for the E-PPR78 approach.
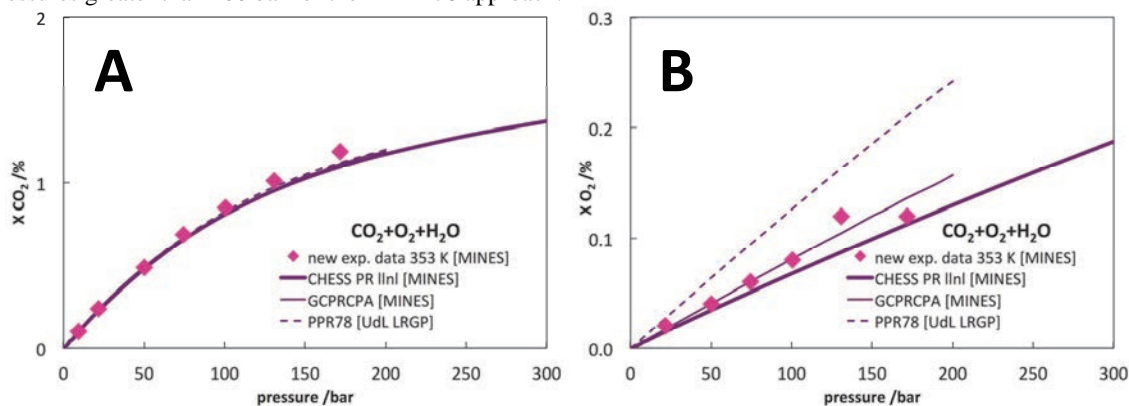
Fig. 4. Aqueous molar fraction (A) CO_2 and (B) O_2 vs. pressure for $CO_2+O_2+H_2O$ system (50%. CO_2 and 50%. O_2) at 353 K. Symbols correspond to new measurements, thin solid lines to GC-PR-CPA model, thin dotted lines to PPR78 model and bold solid lines to CHESS simulations.

6. Simulations of gas+brine systems

Our geochemical code CHESS is also able to simulate the solubility of gases in various saline aqueous solutions. The SIT parameters are usually fitted using experimental data, but we decided at first to use values selected from Millero [20] and to observe how our model will behave then.

6.1. CO₂

The solubility of CO_2 in simple NaCl, KCl, CaCl$_2$ and MgCl$_2$ brines at three temperatures (323, 373 and 423 K) and a pressure of 150 bar were then simulated using CHESS and the simulated solubilities compared with recent results from the literature [35,36] (see Fig. 5).
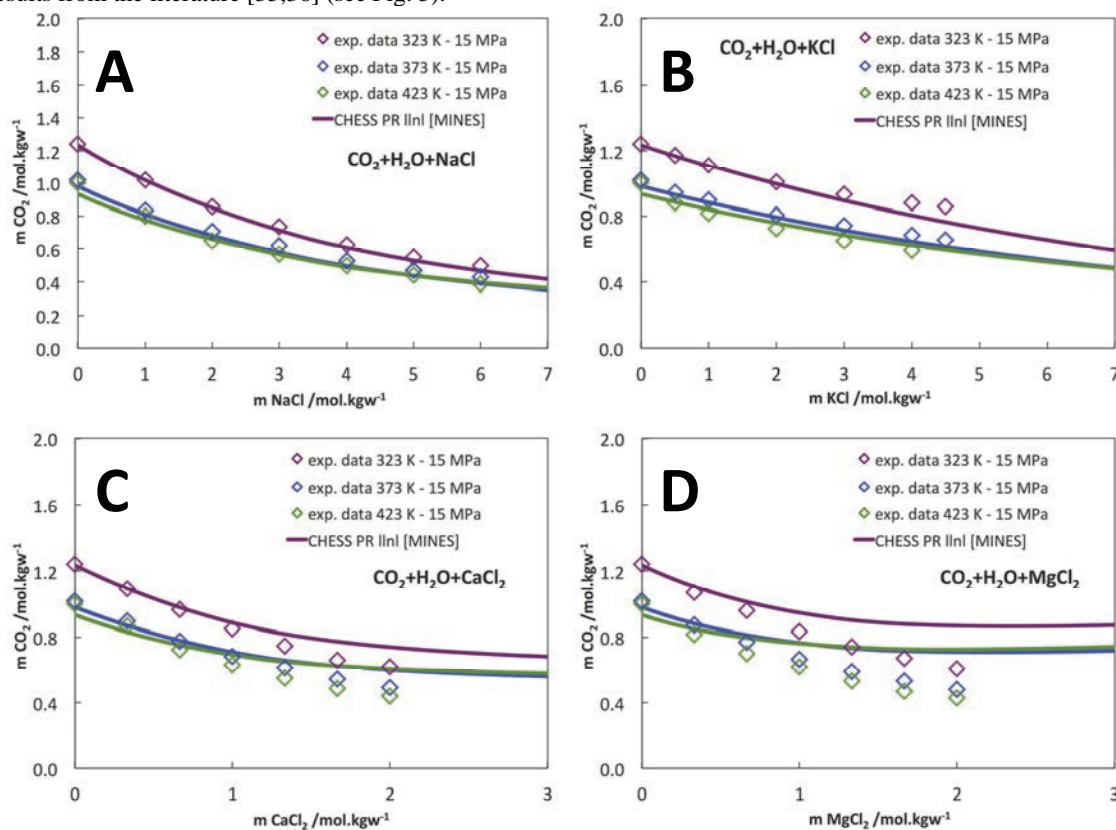

Fig. 5. Aqueous molality of CO_2 at 323, 373 and 423 K, 150 bar in (A) NaCl, (B) KCl, (C) CaCl$_2$ and (D) MgCl$_2$ vs. salt concentrations. Symbols correspond to experimental data [35,36] and bold solid lines to CHESS simulations.

The solubility of CO_2 in NaCl and KCl is well simulated in these conditions up to high salinities up to 6 M. Concerning CaCl$_2$ and MgCl$_2$, simulations are rather good up to 1 M but the simulations differ from the experiments at higher salinities. This surely comes from the SIT parameters that shall be fitted for those species at each temperature and probably salinity.
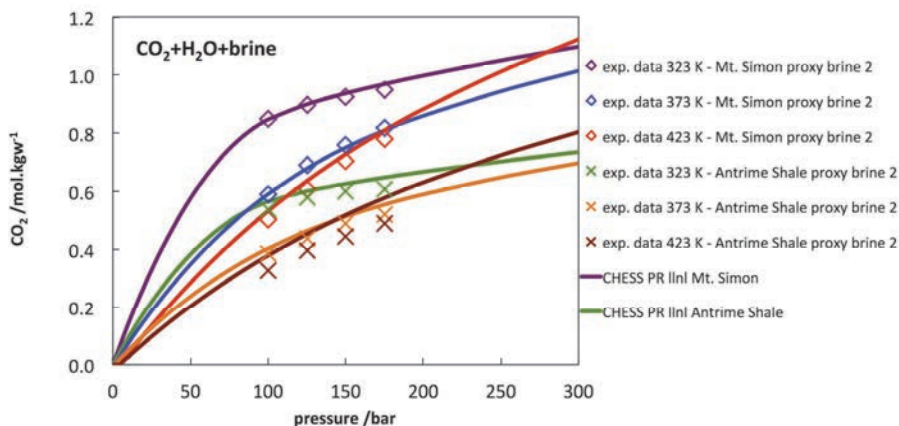
Fig. 6. Aqueous molality of CO_2 at at 323, 373 and 423 K, 150 bar in two synthetic proxy brine vs. pressure. Symbols correspond to experimental data [37] and bold solid lines to CHESS simulations.

The solubility of CO_2 in two synthetic brines, studied experimentally [36], was then simulated (see Fig. 6). The first brine is composed of NaCl 1.0601 mol.kgw^{-1} and $CaCl_2$ 0.2172 mol.kgw^{-1} and represents the Mt. Simon formation. The second one is composed of NaCl 2.9856 mol.kgw^{-1} and $CaCl_2$ 0.6661 mol.kgw^{-1} and represents the Antrim Shale formation. The solubility of CO_2 in those brines is also well simulated in the two cases, whatever the pressure. Our geochemical code CHESS seems then ready to deal with complex brines following our approach.

6.2. Other gases+NaCl

Finally, some experimental solubilities of N_2, CH_4 and O_2 in NaCl brine were also collected and simulated with CHESS (see Fig. 7) with a quite good precision even though the selected data for O_2 correspond to a low pressure case, not relevant of storage sites conditions.
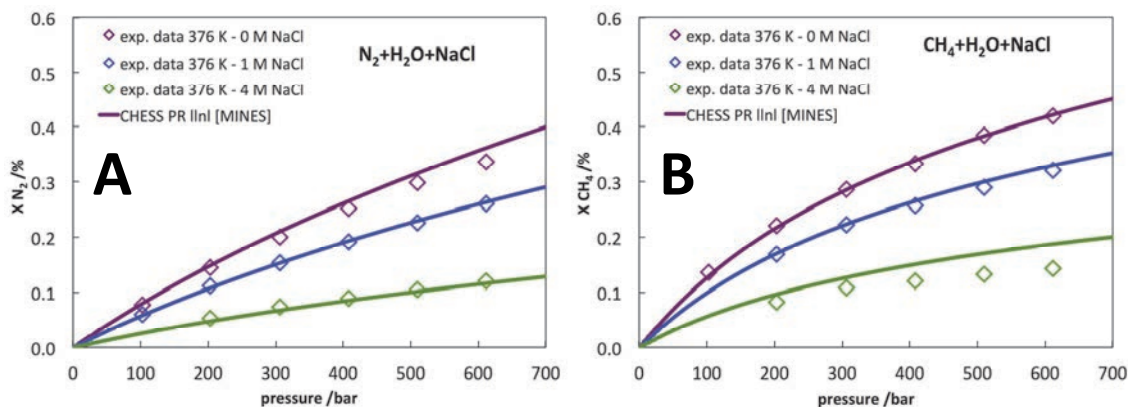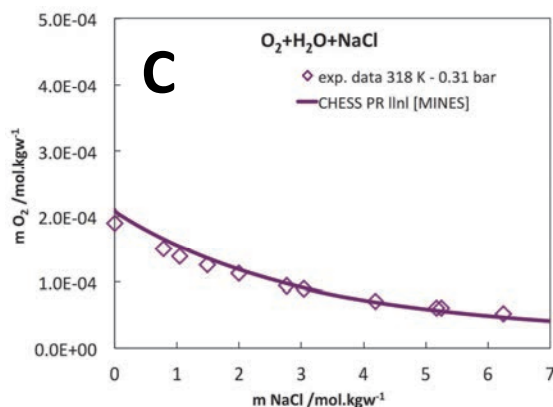
Fig. 7. (A) Aqueous molar fraction of N_2 at 376 K for various NaCl molality vs. pressure, (B) Aqueous molar fraction of CH_4 at 376 K for various NaCl molality vs. pressure and (C) Aqueous molality of O_2 at 318 K and 0.31 bar vs. NaCl molality. Symbols correspond to experimental data [32,38] and bold solid lines to CHESS simulations.

7. Conclusion

In this study, we presented our asymmetric geochemical modeling approach developed within the context of the SIGARRR project to handle gas mixtures+water or brine systems. Experimental data from the literature or data, newly acquired within the project, helped select and/or adjust some parameters, and validate our model as well. We also compared our numerical results with two symmetric processes approaches. The obtained results are very satisfactory and we demonstrated that good numerical results could be obtained with a single geochemical code using a single simple cubic EOS, which is quite convenient for extension to other systems or applications.

Furthermore, this approach should enable us to deal with more complex systems involving rocks in the near future and to reach the final phases of our projects: site-scaled simulations of leakage scenarios with complex gas mixtures and the associated risk analysis, which could also lead to the formulation of first recommendations in terms of geochemically admissible CO_2 flux composition.

It shall be noted that some modifications of the symmetric approach GC-CPA-PR are also in progress to authorize the handling of salts and to offer the possibility of comparisons with the results of the asymmetric geochemical method.

Acknowledgements

References

[1] IEAGHG, Effects of impurities on geological storage of CO_2, *Technical report*, 2011/04.
[2] Creton B, de Bruin T, Le Roux D, Duchet-Suchaux P, Lachet V. *Int J Thermophys* 2014;35:256-76.
[3] Caumon M-C, Sterpenich J, Randi A, Pironon J. *Int J Greenh Gas Control* 2016;47:63-70.
[4] Xu X, Privat R, Jaubert JN, Lachet V, Creton B. *J Supercrit Fluids* 2016, *in press* doi: 10.1016/j.supflu.2016.09.013.
[5] Qian JW Privat R, Jaubert JN, Duchet-Suchaux P. *Energy Fuels* 2013;27: 7150-78.
[6] Xu X, Privat R, Jaubert J-N. *Ind Eng Chem Res* 2015;54:9494-9504.
[7] Hajiw M, Chapoy A, Coquelet C. *Can J Chem Eng* 2015;93:432-42.
[8] Corvisier J. *Goldschmidt Conference,Florence – Italy* 2013.
[9] Corvisier J, El Ahmar E, Coquelet C, Sterpenich J, Privat R, Jaubert J-N, Ballerat-Busserolles K, Coxam J-Y, Cézac P, Contamine F, Serin J-P, Lachet V, Creton B, Parmentier M, Blanc P, André L, de Lary L, Gaucher EC. *Energy Procedia (GHGT-12)* 2014;63:3160–71.
[10] Peng D-Y, Robinson DB. *Ind Eng Chem Fundam* 1976;15:59-64.
[11] Bronsted JN. *J Am Chem Soc* 1922;44:877–98.
[12] Grenthe I, Puigdomenech I. Modeling in Aquatic Chemistry. Nuclear Energy Agency, OECD, Paris, France, 1997.

[13] Yaws CL. Chemical properties handbook: physical, thermodynamic, environmental, transport, safety, and health related properties for organic and inorganic chemicals, New-York: McGaw-Hill; 1999.
[14] Duan Z, Sun R. *Chem Geol* 2003;193:257-71.
[15] Fernandez-Prini R, Alvarez JL, Harvey AH. *J Phys Chem Ref Data* 2003;32:903-16.
[16] Ji X, Lu X, Yan J. *Fluid Phase Equilibr* 2004;222-223:39-47.
[17] Chapoy A, Haghighi H, Tohidi B. *J Chem Thermodyn* 2008;40:1030-7.
[18] Duan Z, Sun R, Liu R, Zhu C. *Energy Fuels* 2007;21:2056-65.
[19] Duan Z, Mao S. *Geochim Cosmochim Acta* 2006;70:3369-86.
[20] Millero F. *Marine Chem* 2000;70:5-22.
[21] Li H, Yan J. *Appl Energy* 2009;86:826-36.
[22] Ziabakhsh-Ganji Z, Kooi H. *Appl Energy* 2014;135:43-52.
[23] Yan W, Huang S, Stenby EH. *Int J Greenh Gas Con* 2011;5:1460-77.
[24] Hou S-X, Maitland GC, Trusler JPM. *J Supercritical Fluids* 2013;73:87-96.
[25] Wiebe R, Gaddy VL, Heins Jr C. *J Am Chem Soc* 1933;55:947-53.
[26] Broden A, Simonson R. *Svensk Papperstidning* 1978;81:541-4.
[27] Kennan RP, Pollack GL. *J Chem Phys* 1990;93:2724-35.
[28] Jung J, Knacke O, Neuschutz D. *Chemie Ing Techn* 1971;43:112-6.
[29] Rumpf B, Maurer G. *Fluid Phase Equilibr* 1992;81:241-60.
[30] Lee JI, Mather AE. *Ber Bunsenges Phys Chem* 1977;81:1020-3.
[31] Gillespie PC, Wilson GM. *GPA Research Report* 1982;RR-48.
[32] O'Sullivan TD, Smith NO. *J Phys Chem* 1970;74:1460-6.
[33] Wiebe R, Gaddy VL. *J Am Chem Soc* 1934;56:76-9.
[34] Valtz A, Chapoy A, Coquelet C, Paricaud P, Richon D. *Fluid Phase Equilibr* 2004;226:333-44.
[35] Zhao H, Fedkin MV, Dilmore RM, Lvov SN. *Geochim Cosmochim Acta* 2015;149:165-89.
[36] Zhao H, Dilmore RM, Lvov SN. *AIChE* 2015;61:2286-97.
[37] Zhao H, Dilmore RM, Allen DE, Hedges, SW, Soong Y, Lvov SN. *Environ Sci Technol* 2015;49:1972-80.
[38] Millero FJ, Huang F. Laferiere AL. *Marine Chem* 2002;78:217-30.