

GHGT-9

CO₂ streams containing associated components - a review of the thermodynamic and geochemical properties and assessment of some reactive transport codes

Jacquemet N.^{a*}, Le Gallo Y.^b, Estublier A.^b, Lachet V.^b, von Dalwigk I.^c, Yan J.^c,
Azaroual M.^a, Audigane P.^a

^aBRGM, avenue Claude Guillemin, 45060 Orléans cedex, France

^bIFP, avenue de Bois Préau, 92852 Reuil-Malmaison cedex, France

^cVattenfall Research and Development AB, Jämtlandsgatan 99, Stockholm, Sweden

Abstract

Modelling of the impact on storage of “CO₂-associated components” has rarely been addressed so far. This review, performed within the European research project CO₂ReMoVe, exposes a selection of CO₂ streams compositions coming from thermal power plants emissions and those injected in pilot sites part of the CO₂ReMoVe project. It highlights the lack of data coming from laboratory experiments to describe properly the physical properties of some relevant gas mixtures. The geochemical impact of only 2 components (SO₂ and H₂S) is evidenced by some geochemical studies. Concerning the numerical modelling, four reactive transport codes (PHREEQC, SCALE2000, TOUGHREACT and COORES) were assessed. Actual limitations lie mainly in the capacity of calculating the physical properties of the whole set of gases (CO₂-O₂-SO₂-N₂-Ar-NO_x-H₂S-COS-CO-H₂-HCl-NH₃-CH₄-C₂H₆-H₂O). The new data acquired within on-going French projects will complete the knowledge of such complex gas mixtures behaviour.

© 2009 Elsevier Ltd. All rights reserved.

Keywords: CO₂ReMoVe, review; gas mixtures; equation of state; experimental data; solubility; geochemical reactions; reactive transport codes

1. Introduction

The impact of other gaseous components (called hereafter “CO₂-associated components”) in the CO₂ stream has rarely been addressed so far, even though the importance has been acknowledged for some time [1]. However CCS (Carbon dioxide Capture and Storage) projects CO₂ streams contain small amounts of other gaseous components. They may have impacts on different stages of a CCS design chain: capture, transportation, injection and storage [2] that need to be taken into account in the qualification process of CO₂ storage projects, e.g. as part of the risk assessment. In the storage phase, streams containing associated components would have different physical

* Corresponding author. Tel.: +33-(0)2-38-64-34-65; fax: +33-(0)2-38-64-37-19.

E-mail address: n.jacquemet@brgm.fr.

properties and geochemical reactivity than a pure CO₂ gas phase [3]. Performing reactive transport simulations including these gaseous components needs appropriate codes that calculate correctly the physical properties of the CO₂-associated components mixtures and the geochemical reactions involving those. The extension of the property databases of the CO₂-associated components mixtures followed by the adaptation/development and calibration of existing codes would be the workflow for their improvement. The CO2ReMoVe (CO₂ geological storage: Research into Monitoring and Verification technology, [4]) project is a consortium of industrial, research and service organizations and will propose new tools to model storage behaviour, applied over a portfolio of storage sites. It includes a task dealing with the CO₂-associated components. As a first step in this research, this paper exposes a state-of-the art of the physical and geochemical properties of the CO₂-associated components as well as the actual capabilities of the codes to account for them. First, the nature and the concentration of the CO₂-associated components in the gas streams generated from thermal power generation plants and occurring at “CO2ReMoVe sites” are exposed. Secondly, the methods of determination of physical properties of gas mixtures and the implications of their changes on storage capacity are presented. Then, we address the geochemistry of associated components and their reactivity with the subsystem, i.e. water-rock. Finally, an inventory of the numerical tools capabilities to take into account the associated components is exposed. It is based on the software user’s guides content, some relevant scientific and technical publications.

2. Identification of CO₂-associated components

2.1. The case of energy-related sources of CO₂

The identification of CO₂-associated components is dependent on the fuels used, the energy conversion processes and the CO₂ capture technologies used in the CO₂ capture plant. In this section, the fuels assumed to be used for the energy conversion are based on German lignite and South African bituminous coal which composition is exposed in [5]. The energy conversion of fuels is based on the following power generation processes: thermal power generation through air-firing and oxyfuel-firing of Pulverised Fuel (PF) like coals; and coal gasification for thermal power generation (e.g. Integrated Gasification Combined Cycle (IGCC)). The CO₂ capture technologies are employed for the corresponding energy conversion processes including: (1) post-combustion CO₂ capture by amine-based absorption processes after air-firing of PF; (2) oxyfuel combustion CO₂ capture based on oxy-coal-firing; (3) pre-combustion CO₂ capture through IGCC processes. Depending on the energy conversion processes, the captured CO₂ streams could be categorised into two types:

- Oxidising CO₂ stream with residual O₂ and sulphur components mainly with SO₂ and varying degrees of inert gases from the air or associated components in oxidant (N₂, Ar) (CO₂ captured from oxyfuel and post combustions),
- Reducing CO₂ stream with almost no residual O₂ and sulphur components mainly with H₂S, COS (carbonyl sulfide) and minor amounts of organic components (CO₂ captured from coal gasification processes such as IGCC).

The captured CO₂ stream from the energy conversion processes are usually cleaned up according to the requirements from the downstream CO₂ processing and the CO₂ quality defined by transport, storage and environmental demands especially on the removal of acidic gases and toxic contaminants. Examples of likely components and compositions of CO₂ mixtures estimated for various capture technologies are exposed in [5]. Beside the main CO₂-associated components cited above, minor amounts of NO_x (NO and/or NO₂), CO, HCl, H₂ and NH₃ are predicted in the both types of gas streams.

2.2. Gas streams compositions in some “CO2ReMoVe sites”

Sleipner [6] and In-Salah [7] are gas fields that contain naturally few percent of CO₂. The first one is an off-shore field located in the Norwegian North Sea and the second one is an on-shore field located in Algeria. At these two sites, the CO₂ is separated from the produced natural gas by an amine absorption process and injected in saline water levels. At the both sites, the CO₂ stream is not pure. At Sleipner, it can contain up to 150 ppm H₂S and up to 5%

non-condensable gases. At In-Salah, the gas stream contains small amounts of methane, ethane and nitrogen and traces of heavier hydrocarbons. The CO₂ streams of these two sites are thus reducing streams.

3. Physical properties of CO₂-associated components mixtures

The presence of associated components in CO₂ stream may affect more or less its behavior from a thermodynamic point of view. The magnitude of the impact is depending on the nature of the associated components and their concentrations. As a result, they may affect the phase equilibrium, the density, injectivity, reactivity with other media, the storage capacity and the Enhanced Oil Recovery (EOR) efficiency, i.e. several of the basic functional requirements of a CO₂ storage project may be affected. Numerical simulators need to integrate powerful formulations to predict Pressure-Volume-Temperature-Composition properties of the CO₂-associated components mixtures.

3.1. Thermodynamic models

3.1.1. Gas phase description

Pure component

In general, for pure components, the Equations Of State (EOS) give good prediction of the fluid properties such as density, volume, etc.... The thermodynamic models are based on cubic EOS's. Standard cubic EOS is the empirical Peng-Robinson and Soave-Redlich-Kwong equation which have to be adjusted on experimental data or from molecular simulations in first approximation. Although usually not the most convenient EOS, the equation of Benedict – Webb – Rubbin modified by Soave, is also used.

Multi-component mixtures

For multi-component mixtures, Duan et al. [8] developed an EOS supposed to be accurate for the mixtures in the system H₂O-CO₂-CH₄-N₂-CO-H₂-O₂-H₂S-Ar. This EOS was favourably compared with experimental data on the mixtures H₂O-CO₂, CO₂-N₂, CH₄-CO₂ and N₂-CO₂-CH₄ on large ranges of temperature and pressure conditions. The uncertainties are in the order of measurement errors within an average error of 1.6% in density. The Duan et al. approach is often used for geothermal systems. Nevertheless numerous databases have to be completed for the CO₂-associated components. Equations of state for pure components can be applied for multi-components mixtures by using mixing rules. The standard mixing rule is the rule of van der Waals. It has been used with success with hydrogen and some inorganic gases (CO₂, N₂, ...) [9]. Nevertheless, it is limited to ideal mixtures. Several others mixing rules have been developed (Panagiotopoulos and Reid [10] and [9]). The different equations of state need to be adjusted to the real fluid in particular the binary interaction coefficient used in the mixing rules. This adjustment requires experiments or molecular simulations.

3.1.2. Aqueous phase description

Concerning the aqueous solution, correlation is usually used to estimate density. It only takes salinity and CO₂ molar volume into account. However, some EOS can describe the dissolution of gas components in the aqueous phase (see section 4).

3.1.3. Transport properties

The viscosity computation rely either on correlations such as Lorentz Bray Clark for hydrocarbon gas or models such as Pedersen et al. [11]. However, these models do not account for the effect of associated components as they were primarily developed for hydrocarbon gas viscosity. Concerning the heat capacity and the thermal conductivity, there seems to be no bibliography on this subject allowing to stating whether or not the existing models are adapted to the CO₂ associated components mixing.

3.2. Measurements

The degree of availability of experimental thermodynamics data on CO₂ mixtures are presented in the Table 1. It appears that data exist for the reductive mixtures but less or not for the oxidative mixtures.

Table 1. Availability of experimental data concerning different CO₂ gas mixtures.

Rich	Less rich	Poor	No data
CO ₂ -H ₂ O	CO ₂ -H ₂ S	CO ₂ -SO _x	CO ₂ -NO _x
CO ₂ -N ₂	CO ₂ -O ₂		
CO ₂ -CH ₄	CO ₂ -H ₂		
CO ₂ -CH ₄ -N ₂	CO ₂ -CO		

3.3. Molecular simulations

Molecular simulation provides an intermediate way between experiments and classical thermodynamic models. It cannot pretend to replace equations of state, which remain necessary for the tremendous number of repeated calculations involved in multiphase fluid flow simulation of reservoirs. It cannot either replace experiments when high accuracy data are needed. Nevertheless molecular simulation may be considered as viable tools providing a qualitative understanding of fluid structure together with a fair prediction of thermodynamic properties, especially useful when classical models are limited by the lack of experimental data. More details are exposed in Ungerer et al. [12] and [13]. Satisfactory predictions have been found on the H₂S-CO₂ system, for which maximum deviations on density are approximately 3% over a large range of composition, pressure and temperature. Nevertheless, thorough studies on this subject are still in progress for accurate results.

3.4. Qualitative effects of the change of physical properties on storage capacity

The presence of associated components in the CO₂ is likely to lower its density and as a consequence lowers the storage capacity available for CO₂ as well as its migration within the reservoir. Their presence may also affect the solubility and subsequently the geochemical reactions. If the reactions lead to a variation of porosity, i.e. change of porosity relative to the initial (prior injection) porosity of the reservoir, the space volume of the storage would be modified as well. The interfacial tension is a function of the gas composition and is directly linked to capillary pressure. If the associated components reduce the interfacial forces between the fluid (water and gas) and the formation rock, the sealing capacity of the cap rock will be reduced and thus the storage efficiency. This has been shown when substituting CO₂ by methane (Chiquet et al. [14] and Chalbaud et al. [15]). Currently, due to the absence of appropriate knowledge it is difficult to quantify precisely the change in the storage capacity due to the presence of associated components in the CO₂ stream. However, the decreased density may reduce the overall storage capacity in the range of yearly injection volumes and lead to that the maximum storage capacity is reached faster than it would be by injection of pure CO₂.

4. Geochemical properties of CO₂-associated components mixtures

4.1. Gas mixture solubility and potential reactivity with water

General formulations of gas solubility can be used as the one exposed in Kervévan et al. [16]:

$$m_{i, aq} = \frac{K_i \Phi_{i, gas} x_{i, gas} P}{\gamma_{i, aq}} \quad (Eq. 1)$$

with $m_{i, aq}$ the molality of the gas species i in the aqueous phase, in mol/kg of water, normalized with respect to a reference molality chosen to be equal to 1 mol/kg of water; K_i the thermodynamic equilibrium constant of the gas dissolution (dimensionless); $\Phi_{i, gas}$ the fugacity coefficient (dimensionless); $x_{i, gas}$ the molar fraction of the species i in the gaseous phase (dimensionless); P the pressure, in bar, normalized with respect to a reference pressure chosen to be equal to 1 bar and $\gamma_{i, aq}$ the activity coefficient (dimensionless). Regarding this formulation, gas species solubility is dependent on temperature, pressure, chemical composition of both the gas (fugacity coefficient) and the brine (activity coefficient) and an accurate thermodynamic equilibrium constant of the dissolution reaction. Appropriate EOS as those of Duan et al. (Duan et al. [17], [18] and Duan and Sun [19]) can be used to calculate the

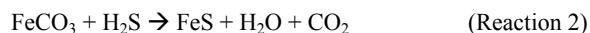
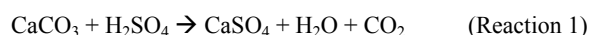
fugacity coefficient of CO₂ in various gas-brine systems. Experimental data are needed for validating a model of CO₂-rich gas mixture solubility. To date, no literature references on CO₂ gas mixtures containing Ar, O₂, SO_x or NO_x have been found. But the individual gas species solubilities in pure water at room conditions are available, e.g. in [20]. The solubility of SO₂ is by example two-to-three orders of magnitude higher than that of CO₂. This high solubility provides large quantities of gas species that can subsequently react with water and rocks.

Some CO₂-associated components are acidic gases (SO₂, SO₃, NO₂, H₂S, ...) that are also redox sensitive species (SO₂, NO₂, H₂S, ...). Their reactivity with water and subsequently minerals will be dependent on pH-Eh (redox potential) conditions of the aqueous system where they are injected.

4.2. Reactivity with minerals: geochemical and reactive transport modeling studies

We restricted our review to 3 papers: Xu et al. [21], Knauss et al. [22] and Gunter et al. [23]. All of those present the impact of the CO₂-associated components H₂S and SO₂ on rock mineralogy of different aquifer types (sandstone and limestone). The assumptions and initial data are summarized in the Table 2.

Gunter et al. [23] performed batch simulations with the code PATHARC.94 (Perkins et al. [24]). The authors point out the following two reaction pathways involving carbonate minerals that illustrate the mineral trapping of H₂SO₄ (species derived from SO₂, see the footnote of the Table 2) and H₂S respectively. The authors mention a possible reduction of porosity linked to these reactions:



Knauss et al. [22] performed 1 dimensional (1D) reactive transport simulations with the code CRUNCH ([25] and Steefel and Yabusaki [26]). The authors estimate that the results of the simulation incorporating H₂S to CO₂ is not significantly different from the results of the simulation with pure CO₂. In contrast, the simulation incorporating SO₂ has significant impact on the mineralogy. Like Gunter et al. [23], the authors mention a precipitation of anhydrite due to the presence of SO₂. Xu et al. [21] performed 1D reactive transport simulations with the code TOUGHREACT (Xu et al. [27]). The results illustrate the dominant geochemical impact of SO₂ relative to CO₂ or H₂S. Indeed, the co-injection of SO₂ induces a very low pH domain (pH~0.6 close to the injection point) around the injection zone. SO₂ is trapped mineralogically by sulphate minerals. A decrease of porosity is related to the precipitation of sulphates.

Table 2. Type of modelling, considered gas, formation name and rock type and formation water chemistry accounted in the literature batch or reactive transport modelling studies dealing with CO₂-associated components.

Reference	Type of modelling	Considered gas species	Name of the formation	Formation water chemistry	Simulated P _{total} , T of the reservoir
G	Batch	CO ₂ , H ₂ SO ₄ [*] , H ₂ S	Glauconitic sandstone aquifer (Alberta basin)	Na, Cl and Ca solution	130 bar-54°C
	Batch	CO ₂ , H ₂ SO ₄ [*] , H ₂ S	Nisku carbonate aquifer	Na, Cl and Ca solution	Idem
K	1D reactive transport	CO ₂ , H ₂ S, SO ₂	Frio Fm. (sandstone) (Texas)	NaCl solution	100 bar-64°C
X	1D (radial) reactive transport	CO ₂ , H ₂ S, SO ₂	Frio Fm. (sandstone) (Texas)	NaCl solution	75°C

Notes: * H₂SO₄ is not a gaseous species but an aqueous species. The authors consider this is derived from the species SO₂ after reaction with water into H₂SO₃ (sulphurous acid) and oxidation by O₂ into H₂SO₄ (sulphuric acid), supposing O₂ is sufficiently present in the medium. G: Gunter et al. [23]; K: Knauss et al. [22]; X: Xu et al. [21].

The geochemical impact of only 2 associated components: H_2S and SO_2 , was investigated through the 3 modelling studies we chose to present. It appears in the three studies that SO_2 has a dominant impact in comparison with H_2S . We hypothesize that after oxidation, it forms sulphurous acid that react with Ca-bearing minerals or Ca simply initially dissolved in formation brine to precipitate sulphate minerals. This precipitation was correlated with a decrease of porosity. Thus, the presence of SO_2 may have impacts on the petrophysical properties (permeability/diffusivity) of the host rock. However, the presented studies contain several assumptions that make the models different than a realistic gas mixture injection scenario:

- in Gunter et al. [23], the flowing of fluid is not accounted (it is a batch study), no gas solubility calculations are performed and no redox reactions are accounted,
- in Knauss et al. [22], the injected fluid is water containing dissolved acid gases (H_2S and SO_2),
- in Xu et al. [21], the injected fluid is a two-phase fluid composed of gaseous CO_2 and water containing dissolved acid gases.

Actually, these assumptions are made to bypass the codes limitations (exposed in the section 5) that lie essentially in the calculation of real CO_2 -rich gas mixtures behavior and solubility. Moreover, formation waters with salinities ranging approximately from 1 to 2 mol/l were considered in the studies and the salinity effect was taken into account by activity corrections following modified Debye-Hückel and B-dot laws for TOUGHREACT and CRUNCH respectively. For such high ionic strengths solutions, other laws like the Pitzer approach are more adapted to correct activities but are currently not available in these codes. Finally, further research is needed to evaluate the impact of other reactive CO_2 -associated components (e.g. NO_x , CO , H_2 and O_2).

5. Capabilities of some geochemical and reactive transport codes

The involvement of CO_2 -associated components in reactive transport simulations needs a suitable statement by the codes of gas mixtures physical properties, solubility and redox reactions. The capabilities of five codes that are likely to be used by the project partners are assessed here. They are: PHREEQC (Parkhurst and Appelo [28]), SCALE2000 v4.0 (under development) (Azaroual et al. [29] and [30]), TOUGHREACT (with the thermodynamic and flow module ECO2N) (Xu et al. [27] and [31]) and COORES (Le Gallo et al. [32] and Trenty et al. [33]). It has to be noted that other codes exist.

Despite PHREEQC has the more complete chemical database and accounts for the redox reactions, this code has a shortcoming: it does not include a real gas approach for solubility calculation (Table 3). SCALE200 includes a real gas approach for calculating the solubility of the mixture CO_2 - H_2S - H_2O - CH_4 - N_2 but the redox reactions are not accounted. The chemical database of TOUGHREACT is quite complete and it deals with redox reactions but the only gas mixture it considers for solubility calculation via a real gas approach is CO_2 - H_2O (CO_2 - CH_4 mixtures are also handled but by the thermodynamic and flow module EOS7C). The COORES chemical database is also quite complete and redox reactions are taken into account. This code can calculate potentially any mixture solubility since the components are defined by the user. The solubility is determined via tabulations and hence depends on the available data.

Table 3. Codes capabilities for solubility calculation via real gas approach and for redox reactions.

	PHREEQC	SCALE2000	TOUGHREACT	COORES
Gas mixture for which real gas assumption is used for solubility calculation	None	CO_2 - H_2S - H_2O - CH_4 - N_2	CO_2 - H_2O	*
Redox reactions calculation	Yes	No	Yes	Yes

*: gas solubility is tabulated as function of pressure and temperature. This implies that the thermodynamic properties are known and available.

5.1. Needs for future developments

The limitations of the available numerical codes in the CO₂ReMoVe teams are essentially linked to the lack of relevant measurement data. Some limitations are also due to the inherent difficulties of theoretical and/or empirical approaches integrated as, for example, the integration of the water effect in the Peng-Robinson EOS which is still a challenge. The Duan et al. approach is more relevant for the integration of water but it still needs more experimental measurements. Another way which can be explored is perhaps attempting some combination of the EOS approaches and developing hybrid methodologies and integrating more flexible algorithms. There is some recent development of new approaches as the Cubic-Plus-Association (Kontogeorgis et al. [34]), Statistical Associating Fluid Theory EOS for the gas phase and NRTL (Non-Random Two Liquid) activity coefficient model for the electrolytic systems in the water-rich liquid phase.

6. Conclusion

We exposed estimated compositions of CO₂-associated components mixtures generated from thermal power generation plants. The mixtures that are currently injected at “CO₂ReMoVe sites” (Sleipner and In-Salah) deal with CO₂ streams from natural gas purification processing and are thus different than those captured from thermal power generation. The thermodynamic properties of multi-component gas mixtures can be modelled by using standard cubic EOSs with mixing rules or by using the EOSs of Duan et al. The parameters of the EOSs have to be calibrated on experimental data. Unfortunately, only some binary and few ternary gas mixtures are informed. Numerous experimental databases have to be completed to describe the diversity of CO₂-associated components mixtures. Molecular simulations can be an alternative to experiments as they can be used to determine fluid properties especially when experimental data are scarce. Little or no data exist on transport properties, heat capacity, solid-gas interfacial tensions and thermal properties of the multicomponent gas mixtures. Nevertheless, acquisition of data is planned in some projects in 2008. Data on CO₂-associated components individual solubilities are exposed as well as their chemical properties within water (briefly). It appears that SO₂ is very soluble and very acid (as the NO₂) compared to CO₂. Some geochemical modelling studies evidenced that the SO₂ reacts with mineral matrix of rocks to precipitate sulphates minerals. However, these studies are based on assumptions to bypass the codes limitations. These lie in the calculation of the physical properties, the solubility and finally in transporting multicomponent gas mixtures. These limitations are actually due to the lack of relevant data on physical properties and solubility of CO₂-associated components mixtures rather than algorithms limits. The reactions involving the CO₂-associated components can be potentially described by the portfolio of the five geochemical/reactive transport codes assessed (PHREEQC, SCALE2000, TOUGHREACT and COORES). But none of these numerical codes is currently integrating the complete system (CO₂-O₂-SO₂-N₂-Ar-NO_x-H₂S-COS-CO-H₂-HCl-NH₃-CH₄-C₂H₆-H₂O) in the relevant conditions of CCS. Implementations of new formulations in the codes would be premature as PVT_x experimental data are first needed. Undergoing French national projects (“ANR gaz annexes”) will improve the knowledge. The next step of research in the task WP2.2.2b of CO₂ReMoVe will focus rather on current codes applications to the “CO₂ReMoVe sites”. Regarding the code limitations exposed above, hypotheses will be formulated to account for the CO₂-associated components in the simulations.

Acknowledgements

The authors thank the CO₂ReMoVe consortium for permission to publish this work.

References

1. M. Anheden, A. Andersson, C. Bernstone, S Eriksson, J. Yan, S. Liljemark and C. Wall, CO₂ quality requirement for a system with CO₂ capture, transport and storage, *In: GHGT-7 proceedings*, Vancouver, 2004.
2. IPCC (Intergovernmental Panel on Climate Change), *IPCC Special Report on Carbon dioxide Capture and Storage*, Cambridge University Press, New York, 2005.
3. IEA GHG, *Impact of Impurities on CO₂ capture, Transport and Storage*, Report Number PH4/32, 2004.

4. CO2ReMoVe, <http://www.co2remove.eu/>, 2008.
5. CO2ReMoVe, *CO₂ streams containing associated components - a review of the thermodynamic and geochemical properties and assessment of some reactive transport codes*, Deliverable 2.2.2B, 2008.
6. P. Audigane, I. Gaus, I. Czernichowski-lauriol, K. Pruess and T. Xu, Two-dimensional reactive transport modeling of CO₂ injection in a saline aquifer at the sleipner site, north sea, *Am. J. Sci.* 307 (2007) 974.
7. CO2ReMoVe, *In Salah performance assessment basis*, Deliverable D2.3.1, 2007.
8. Z. Duan, N. Moller and J. H. Weare, A general equation of state for supercritical fluid mixtures and molecular dynamics simulation of mixture PVTX properties, *Geochim. Cosmochim. Acta* 60 (1996) 1209.
9. S. I. Sandler, *Models for thermodynamic and phase equilibria calculations*, Marcel Dekker, New York, 1994.
10. A. Z. Panagiotopoulos, R. C. Reid, New mixing rule for cubic equations of state for highly polar, asymmetric systems, *ACS Symp. Ser.* 300 (1986) 571.
11. K. S. Pedersen, A. Fredenslund, P. L. Christensen and P. Thomassen, *Chem. Eng. Sci.* 39 (1984) 1011.
12. P. Ungerer, A. Wender and G. Demoulin, Application of Gibbs Ensemble and NPT Monte Carlo Simulation to the Development of Improved Processes for H₂S-rich Gases, *Mol. Simulat.* 0, (2004) 1.
13. P. Ungerer, V. Lachet and B. Tavittian, Applications of Molecular Simulation in Oil and Gas Production and Processing, *Oil Gas Sci. Technol.* 61 (2006) 387.
14. P. Chiquet, D. Broseta and S. Thibeau, *Capillary Alteration of Shaly Caprocks by Carbon Dioxide*, SPE 94183 (2005).
15. C. Chalbaud, M. Robin and P. Egermann *Interfacial tension data and correlations of brine-CO₂ systems under reservoir conditions*, SPE 102918 (2006).
16. C. Kervéan, M. Azaroual and P. Durst, Improvement of the calculation accuracy of acid gas solubility in deep reservoir brines: application to the geological storage of CO₂, *Oil Gas Sci. Technol.* 60 (2005) 357.
17. Z. Duan, N. Moller and J. H. Weare, An equation of state for the CH₄-CO₂-H₂O system : I. Pure systems for 0 to 1000° C and 0 to 8000 bar, *Geochim. Cosmochim. Acta* 56 (1992) 2605.
18. Z. Duan, N. Moller and J. H. Weare, An equation of state for the CH₄-CO₂-H₂O system : II. Mixture from 50 to 1000° C and 0 to 1000 bar, *Geochim. Cosmochim. Acta* 56 (1992) 2619.
19. Z. Duan and R. Sun, An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 5333 K and from 0 to 2000 bar, *Chem. Geol.* 193 (2003) 257.
20. NIST Chemistry Webbook, available at <http://webbook.nist.gov/chemistry>, 2006.
21. T. Xu, J.A. Apps, K. Pruess and H. Yamamoto, Numerical modeling of injection and mineral trapping of CO₂ with H₂S and SO₂ in a sandstone formation, *Chem. Geol.* 242 (2007) 319.
22. K. G. Knauss, J. W. Johnson and C. I. Steefel, Evaluation of the impact of CO₂, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO₂, *Chem. Geol.* 217 (2005) 339.
23. W.D. Gunter, E. H. Perkins and I. Hutcheon, Aquifer disposal of acid gases: modelling of water-rock reactions for trapping of acid wastes. *Appl. Geochem.* 15 (2000) 1085.
24. E.H. Perkins, W.D. Gunter, H.W. Nesbitt and L.C. St-Arnaud, Critical review of classes of geochemical models adaptable for prediction of acidic drainage from mine waste rock, *In: 4th Int. Conf. on Acid Rock Drainage Proceedings*, Vancouver, 1997.
25. C.I. Steefel, *GIMRT, version 1.2: Software for modeling multicomponent, multidimensional reactive transport, User's Guide*, Lawrence Livermore National Laboratory, 2001.
26. C.I. Steefel and S.B. Yabusaki, *OS3D/GIMRT, Software for multicomponent-multidimensional reactive transport: User's Manual and Programmer's Guide*, Pacific Northwest National Laboratory report, 1996.
27. T. Xu, E. L. Sonnenthal, N. Spycher and K. Pruess, *TOUGHREACT user's guide: A simulation program for non-isothermal multiphase reactive geochemical transport in variable saturated geologic media*, Lawrence Berkeley National Laboratory report, 2004.
28. D. L. Parkhurst and C. A. J. Appelo, *User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, Water-Resources Investigations report, U.S. Geological Survey, 1999.
29. M. Azaroual, C. Kervéan, P. Durst, M.-V. Durand and S. Brochot, *SCALE2000 (v3.1), manuel d'utilisation*, BRGM, 2004.
30. M. Azaroual, C. Kervéan, M.-V. Durand and P. Durst, SCALE2000: reaction-transport software dedicated to thermokinetic prediction and quantification of scales applicability to desalination problems, *Desalination* 165 (2004) 409.
31. K. Pruess, ECO2N: a TOUGH2 fluid property module for mixtures of water, NaCl and CO₂, Lawrence Berkeley National Laboratory report, 2005.
32. Y. Le Gallo, L. Trenty, A. Michel, S. Vidal-Gilbert, T. Parra and L. Jeannin, Long-term flow simulations of CO₂ storage in saline aquifer, *In: Proceedings of International Conference on Greenhouse Gas Control Technologies*, Trondheim, 2006.
33. L. Trenty, A. Michel, E. Tillier and Y. Le Gallo, A sequential splitting strategy for CO₂ storage modelling, *In: Proceedings of the 10th European Conference on the Mathematics of Oil Recovery*, Amsterdam, 2006.
34. G.M. Kontogeorgis, E. Voutsas, I. Yakoumis and D.P. Tassios, An equation of state for associating fluids, *Ind. Eng. Chem. Res.* 35 (1996) 4310.