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Role of impurities on CO₂ injection: experimental and numerical simulations of thermodynamic properties of water-salt-gas mixtures (CO₂ + co-injected gases) under geological storage conditions

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Abstract

Regarding the hydrocarbon source and CO₂ capture processes, fuel gas from boilers may be accompanied by so-called "annex gases" which could be co-injected in a geological storage. These gases, such as SO_x, NO_x, or oxygen for instance, are likely to interact with reservoir fluids and rocks and well materials (casing and cement) and could potentially affect the safety of the storage.

However, there are currently only few data on the behaviour of such gas mixtures, as well as on their chemical reactivity, especially in the presence of water. One reason for this lack comes from the difficulty in handling because of their dangerousness and their chemical reactivity. Therefore, the purpose of the "Gaz Annexes" project was to develop new experimental and analytical protocols in order to acquire new thermodynamic data on these annex gases, *in fine* for predicting the behaviour of a geological storage of CO₂ + co-injected gases in the short, medium and long terms.

This paper presents the main results from the "Gaz Annexes" project concerning acquisition of PVT experimental and pseudo-experimental data to adjust and validate thermodynamic models for water / gas / salts mixtures as well as the possible influence of SO₂ and NO on the geological storage of CO₂.

The "Gaz Annexes" project gives new insights for the establishment of recommendations concerning acceptable content of annex gases.

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Co-injected gases; SO₂; NO; CO₂ storage

1. Introduction

Regarding the hydrocarbon source and CO₂ capture processes, fuel gas from boilers may be accompanied by so-called "annex gases" which could be co-injected in a geological storage. These gases, such as SO_x, NO_x, or oxygen for instance, are likely to interact with reservoir fluids and rocks and well materials (casing and cement) and could potentially affect the safety of the storage.

However, there are currently only few data on the behaviour of such gas mixtures under conditions of CO₂ capture and storage, as well as on their chemical reactivity, especially in the presence of water. One reason for this lack comes from the difficulty in handling because of their dangerousness and their chemical reactivity. Therefore, the purpose of the "Gaz Annexes" project was to develop new experimental and analytical protocols in order to acquire new thermodynamic data on these annex gases, *in fine* for predicting the behaviour of a geological storage of CO₂ + annex gases in the short, medium and long terms.

This paper presents the main results from the "Gaz Annexes" project in term of influence of co-injected gases on the possible evolution of geological storage of CO₂ and gives new insights for the establishment of recommendations concerning acceptable content of annex gases.

The "Gaz Annexes" project is organized from two main approaches: the first is based on the acquisition of PVT experimental and pseudo-experimental data to adjust and validate thermodynamic models for water / gas / salts mixtures while the second describes the influence of two important co-

injected gases that are SO₂ and NO. This paper summarizes the main analytical, experimental and numerical developments performed during the project.

2. Acquisition of PVT experimental and pseudo-experimental data on annex gases and CO₂

One of the goal of the project was to acquire new thermodynamic data (solubility, phase envelopes, densities) on water/gas/salt systems including annex gases. Scientific and technical challenges resided in corrosive and hazardous gas handling. The new devices developed in this project are based on Raman micro-spectrometry used for the analysis of the fluid phases at high pressure and high temperature. Raman is coupled to capillary techniques, fluid inclusions and probes for in situ analysis in an autoclave.

Monte-Carlo simulations as well as chromatographic analysis based on the "static-analytical" method generated new thermodynamic data for systems containing NO, SO₂, O₂, N₂, and Ar.

Finally, geochemical codes were updated with these data and confronted with the experimental results obtained in the laboratory on mineral/water/annex gases systems under geological storage conditions.

The results obtained in the framework of the project and concerning the acquisition of new data on annex gases and CO₂ under geological conditions of storage can be described according to 5 items.

2.1. Semi-quantitative budget of gases possibly co-injected from different industries and capture processes

The purpose of this literature review was to identify a list of minor compounds potentially present in the gas mixture to be sequestered in a CCS scheme. If the nature of the industrial sector has to be considered, the type of capture chosen and the constraints of separation and transport used also lead to a wide range of situations. An overview is outlined in Table 1.

Table 1. Range of concentrations of the different compounds possibly co-injected with CO₂ as a function of the type of industry and capture processes

Compound	Range of concentration in the mixture before injection	Observations
CO ₂	75 - 99 %	
N ₂	0 - 25%	Oxycombustion : max 4%. Postcapture: broader range due to less efficient process
O ₂	0 - 4%	Max content if oxycombustion
Ar	0 - 6%	Max content if oxycombustion
H ₂ O	5 - 500 ppmv	Residual content imposed by transport constraints
SOx	0 - 3%	Function of the pre-treatment process
H ₂ S	0 - 1%	Precombustion, reduced atmosphere, (gasification of coal, petroleum coke...)
NOx	0 - 1%	Function of the pre-treatment process
H ₂	< 1%	For precombustion or steel industry
CO	<1%	For precombustion or steel industry
Hg	several ppm	Specific of coal
Formate	several ppm	Capture process like MEA absorption

Among the possible co-injected gases, SO₂ and NO were chosen to perform deeper studies. The reason is that SO₂ and NO are known for their important chemical reactivity as strong acids when solubilized in water and as oxidizing agents.

2.2. Development of new analytical and experimental methods

The development of new analytical and experimental methods to obtain data on CO₂ and annex gases is well illustrated by the new vapor-liquid equilibrium cell for handling SO₂ [1], the construction of the isochore "capillary" line for handling micro-volumes of hazardous gases, the implementing of *in situ* Raman spectrometric measurements at high pressure and high temperature for different solubilities and co-solubilities in the system water/CO₂/salt (Fig. 1), and the development of experiments in gold capsules for testing the reactivity of SO₂ and NO [2].

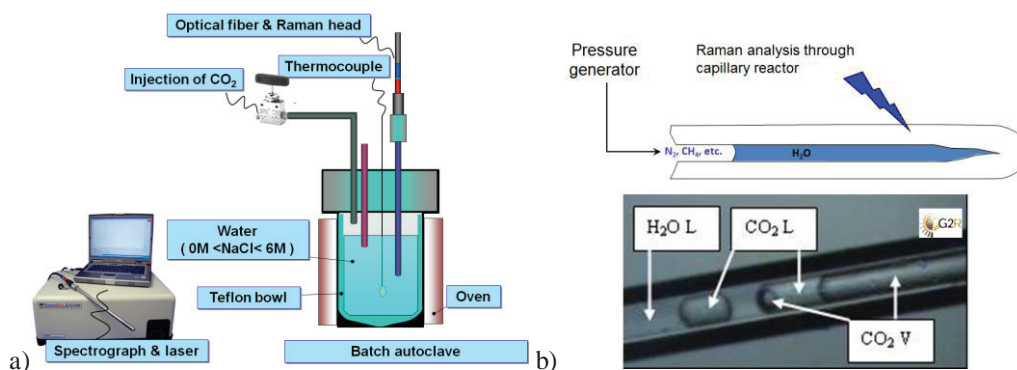


Fig. 1. a) Experimental design for in situ Raman analysis of both gas and aqueous phase; b) The capillary technique allowing to handle hazardous gases at high pressure and temperature (inner diameter of capillary is 100 μm)

2.3. Acquisition of experimental and pseudo-experimental data

This part describes the main results obtained on CO₂ and annex gases under geological storage conditions (high pressure and temperature). The systems, procedures and experimental conditions are summarized in Table 2.

Table 2. Summary of the systems studied in the “Gaz Annexes” project

Method	Systems	Temperature	Pressure
in situ Raman	brine : NaCl, KCl, CaCl ₂ 0 to 4M	25 to 200 °C	Psat (1 to 20 bar)
	Pure CO ₂	150°C	20-200 bar
Capillary	H ₂ O-CO ₂ -salt	20-400 °C	1-1000 bar
Synthetic inclusions	H ₂ O-salt-NO, H ₂ O-salt-SO ₂ , NO and SO ₂	150 °C	100 bar
EOS	CO ₂ + n-heptane	5 – 140 °C	20-150 bar
	CO ₂ + isooctane		
	CO ₂ + 2,5 dimethyl hexane		
	CO ₂ + 3 methyl pentane +H ₂ O		
Chromatography static-analytical	SO ₂ -O ₂ , SO ₂ -N ₂ , SO ₂ -Ar, SO ₂ -N ₂ -Ar,	50-140 °C (binary)	20-200bar (binary)
	SO ₂ -N ₂ -O ₂	50-100 °C (ternary)	100-190 bar (ternary)

In this study data from vapor-liquid equilibrium and / or solubility obtained via pseudo-experimental methods (Monte Carlo simulations) for binary systems SO_2/O_2 , SO_2/N_2 , $\text{SO}_2/\text{H}_2\text{O}$, $\text{O}_2/\text{H}_2\text{O}$ and $\text{N}_2/\text{H}_2\text{O}$ were acquired. First, the potentials of pure compounds were studied. The ability of models for pure compounds used to predict thermodynamic properties such as density, enthalpy of vaporization and the saturation vapor pressure was checked. The comparison between simulation and experimental data shows a good agreement. In a second section, Monte Carlo simulations were carried out in order to determine the compositions and densities of liquid and vapor phases for SO_2/O_2 and SO_2/N_2 binary mixtures. The results of simulations were compared with experimental data [2]. The agreement between the measured and simulated data is good. The contribution of molecular simulation yielded new points usually not accessible experimentally, for instance for the system SO_2/N_2 with pressures up to 1000 bar. In addition, molecular simulations generated new density values for SO_2/O_2 and SO_2/N_2 binary systems. In a last time, results on gas solubilities in water were calculated. The solubility of SO_2 in H_2O and the Henry constants of O_2 and N_2 in H_2O were reproduced by molecular simulation in good agreement with experimental data.

In parallel to pseudo-experimental methods, experiments dedicated to the acquisition of new data on vapor-liquid equilibrium gas by 'static-analysis' chromatography were performed. New experimental data were acquired on the following systems:

- Binary N_2 - SO_2 , Ar- SO_2 and O_2 - SO_2
- Ternary O_2 - N_2 - SO_2 and Ar- N_2 - SO_2

The investigated range of temperature is 50-140°C (binary) and 50-100°C (ternary). The pressures vary from 20 to 200 bar (binary) and from 100 to 190 bar (ternary). The experimental results were compared to the Monte Carlo simulations [2].

2.4. Review of thermodynamic properties of the gases of interest and adaptation of equations of state

This study is based on the thermodynamic properties of the gases of interest in the context of CO_2 storage and on the adaptation of equations of state, especially for systems containing water and hydrocarbons. The systems CO_2 + n-heptane, CO_2 + isooctane, CO_2 + 2,5 dimethyl hexane, and CO_2 + 3 methyl pentane were studied between 5 and 140 °C and 20 and 150 bar. The results are extensively commented in [3-6].

2.5. Chemistry of gas in aqueous solution

This study was focused on the chemistry of CO_2 and annex gases in aqueous solution by identifying the set of chemical reactions in systems containing CO_2 , SO_2 and NO . A new method for in situ measurement of pH carbonate environment was developed.

Annex gases show a complex chemistry in solution still poorly documented in literature, in particular the disproportionation reactions in systems containing sulfur oxides or nitrogen oxides. For the most part, in addition to their acidic action, systems containing sulfur oxides or nitrogen oxides play an important role in controlling the redox potential of the system in conditions of CO_2 geological storage. Besides, Raman spectroscopy is used to study the speciation of carbonates in aqueous solution. Activity of ions, deduced from the spectral analysis, was used to determine the pH of the solution. The knowledge of the speciation of carbonates should be improved by analyzing the influence of the initial concentration of carbonate and salinity on the balance between carbonate and bicarbonate ions. After calibration of Raman signal of both carbonate and bicarbonate ions, neutral to weakly basic solutions were analyzed *in situ*

under high pressure and high temperature. The use of specific pH probes was then avoided, which prevented the sampling of solution that disrupted the system during the experiment.

The highlights are the development of new experimental and analytical techniques to investigate the properties of hazardous and corrosive gases (SO₂, NO, H₂S). These techniques bring new results in the geological storage domain and can also be extended to other areas of high pressure and temperature (geological applications), but also to other gases (CO, NO₂, CH₄, etc.).

3. The specific case of SO₂ and NO

The success of the geochemical simulation is linked to the evolution and improvement of geochemical codes as well as the confrontation of experimental results with those from simulation. In this context an experimental work based on the reactivity of SO₂ in the presence of calcite was chosen as a reference (PhD thesis Stéphane Renard (ADEME-TOTAL) [2]). These experiments were modeled by different partners (TOTAL, BRGM, IFPEN, MINES Paristech) using three different calculation codes (ARXIM, CHESS and PHREEQC). A non-classical use of these modeling tools is necessary due to the very acidic, high temperature and high pressure conditions of such experiments. The comparison of modeling was mainly focused on equilibrium constants, the activity coefficients and the method used to consider the gas phase. The experimental study shows the disproportionation of SO₂ to give sulfate and elemental sulfur, dissolution of calcite and precipitation of anhydrite. Numerical results confirm that these three reactions are thermodynamically favorable in experimental conditions. Depending on reaction progress, thermodynamic calculations predict formation of elemental sulfur and/or hydrogen sulfide although this last component is not observed in experiments. At low SO₂/calcite ratio, calcite is under-saturated but still present after one month of experiment, showing that thermodynamic equilibrium is not reached. Global reactivity of the system seems to be limited by calcite passivation associated with anhydrite precipitation. Passivation leads to a decrease of accessibility of calcite surface. It operates both on surface reactivity and on the diffusive transport between the aqueous solution and the surface, this second mechanism being known to control the rate of calcite dissolution at low pH.

The modeling results obtained by the different teams are often in good agreement, but their comparison has highlighted some limitations: (1) differences in the thermodynamic databases show the importance of using an updated database including recent data on minerals solubility, (2) most models are limited to low ionic strengths and at higher ionic strengths, the Pitzer formalism necessitates to simplify the geochemical system, (3) considering a mixture of ideal gases in numerical codes is an important approximation under high pressure conditions and one of the main limitations of the study of co-injected gases with CO₂.

To conclude, the “Gaz Annexes” project brought many new results on thermodynamic properties and reactivity of highly reactive gases. As an example, SO₂ and NO were extensively studied under geological conditions of storage in this project. Disproportionation reactions leading to the formation of nitric and sulphuric acids were highlighted, and the reactivity of such gases was tested both experimentally [2, 7, 8] and numerically. The comparison of data from geochemical modelling with experimental results show a good agreement between the two approaches. It validates the use of geochemical modelling for the prediction of the long-term evolution of the storage.

4. Conclusion

The results obtained in particular on SO₂ and NO are of crucial interest for manufacturers who have to inject mixtures containing these gases in geological reservoirs. The reactivity of such gas with well materials, reservoir rocks and caprocks was investigated during this project. Moreover, their behavior under high pressure is particularly complex with spontaneous redox reactions leading to the production of

new species which have to be taken into account in the numerical simulations. In addition, this project has enabled partner laboratories to place themselves as leaders in the acquisition of data on CO₂ and co-injected gases under geological storage conditions. The experience will be extended to new systems and new physico-chemical conditions. Finally, geochemical codes have been tested in extreme conditions and successfully compared with experimental results.

To conclude and sum up, the “*Gaz Annexes*” project has contributed:

- to inventory the gases that could be possibly co-injected with CO₂,
- to build experiments to measure gas solubility in aqueous medium,
- to improve equations of state for these gases helping to better understand the water/gas system,
- to provide geochemical simulations and to initiate the development and/or improvement of several reaction-transport code (PHREEQC, ARXIM, CHESS and HYTEC),
- to provide a first experiment of the reaction between a gas mixture of CO₂-SO₂-O₂-N₂, a brine and different minerals characteristics of reservoir rocks and caprock from a storage site.

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