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Experimental determination of CO₂ solubility in brines at high temperatures and high pressures and induced corrosion of materials in geothermal equipment

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Global warming has been observed for many years and has brought about important climate change. A major cause of global warming is the steady increase of greenhouse gases emissions and particularly CO₂. One of the objectives of the Paris agreement, whose purpose is to fight against global warming, is to keep the increase of the general temperature below 2°C by 2100 [1].

To lessen the emissions of this greenhouse gas and thus reduce global warming, the capture, recovery and storage of carbon dioxide is an increasingly studied option. Carbon dioxide can be stored in deep saline formations which have a large capacity. Nevertheless, the amount of carbon dioxide dissolved in the water depends on the pressure, temperature and composition of the water.

Another studied option to reduce global warming is to develop renewable energy. The use of geothermal energy in the world is still in development, both for the production of electricity and heat. In 2015, the total energy produced by geothermal power throughout the world was around 74,000 GWh [2]. The deep geothermal energy to produce electricity or heat for large complexes is under development. In France, more precisely in the Upper Rhine Graben region, several projects have been carried out, in Soultz-sous-Forêts for instance. The aim is to recover a hot fluid from deep subsoil. This fluid passes through a heat exchanger where the energy is released to a secondary fluid. The cooled geothermal fluid is then re-injected into a second well [3]. It is very important to have a good knowledge of the fluid behaviour to better design equipment and reduce the cost of the installations. Another crucial point is to prevent installations from corrosion. Material choice remains difficult due to the fluid composition, the operating temperatures and pressures and the presence of acid gas dissolved.

A good knowledge of the liquid-vapour equilibrium, particularly gas solubility, for these two different applications is essential. Models allowing the prediction of carbon dioxide solubility in brines have been previously developed. However, they are fitted from experimental data. Experimental measurements of carbon dioxide in brines are therefore needed. The determination of gas solubility at high temperatures and pressures is quite complex. Although many data are available in the literature for the CO₂ solubility in pure water or single salt solutions, data for carbon dioxide solubility in mixed-salt solutions are still missing. The aim

of this study was to use a simple method developed in previous papers [4, 5] to determine the carbon dioxide solubility in brines at high temperatures and high pressures.

CO₂ solubility has been measured in two synthetic brines. The composition of the brines was based on the Soultz-sous-Forêts (Upper Rhine Graben) water. The fluid of Soultz is classified as Na-Ca-Cl type with a TDS (Total Dissolved Solids) around 90 g/L. The first brine consists in a mixture of NaCl and CaCl₂ salts, respectively at concentration of 1.2 mol/kgw and 0.2 mol/kgw. The second brine is made of 1.2 mol/kgw of NaCl, 0.2 mol/kgw of CaCl₂ and 0.1 mol/kgw of KCl. Both CO₂-H₂O-NaCl-CaCl₂ and CO₂-H₂O-NaCl-CaCl₂-KCl systems have been studied at three temperatures: 323, 373 and 423 K and up to 20 MPa.

A high pressure and high temperature apparatus has been used to reproduce the subsol conditions and obtain the thermodynamic equilibrium. The sampling process is based on the trapping method. It consists in withdrawing an aqueous sample of the equilibrium cell in a syringe containing soda. Then, carbon dioxide measurements have been carried out by conductimetric titration coupled with pH measurements.

48 experimental solubility data have been obtained. The results show that the carbon dioxide solubility increase when the pressure increase. On the other hand, an increase in temperature or salinity implies a decrease of the gas solubility. Experimental results have been compared with two different models (PhreeSCALE and PSUCO₂). This comparison between measured and calculated values show a good agreement (Figure 1).

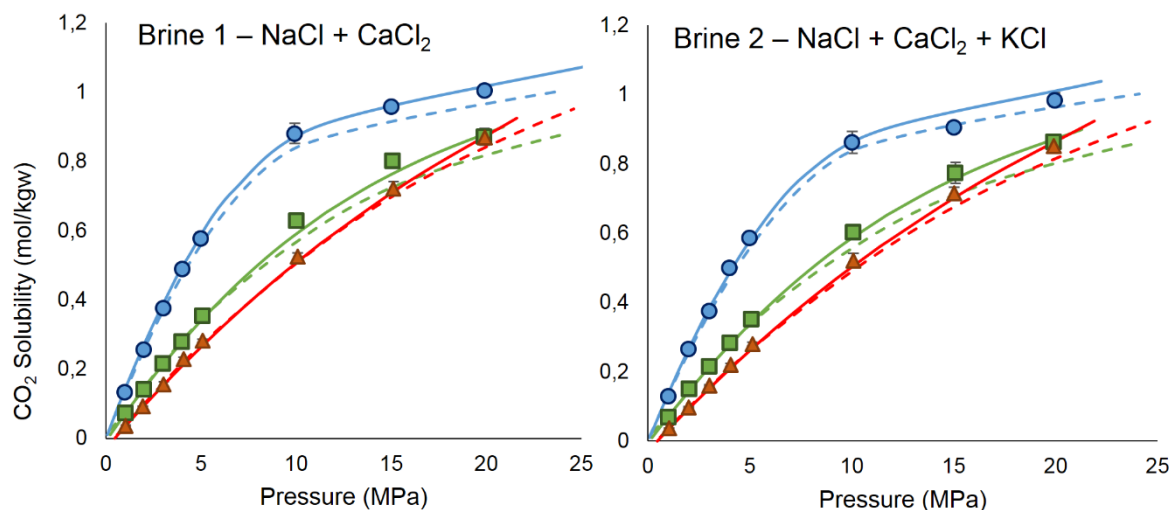


Figure 1: Comparison between experimental data obtained in the two synthetic brines at 323 (●), 373 (■) and 423 K (▲) up to 20 MPa and predicted CO₂ solubility obtained with PhreeSCALE (solid line) and PSUCO₂ model (dashed line)

The second part of this work consists in studying the material corrosion in these particular environments (high temperature, high pressure, brines). The aim of this study is to observe if the corrosion process induced by geothermal fluid occurs on several materials. In such case, the next step is to better understand the corrosion phenomena. Previous studies conducted at the

Soultz-sous-Forêts geothermal power plant have allowed a first step towards the understanding of corrosion processes and mechanisms [6, 7, 8].

In this study, a corrosion pilot (Figure 2) has been developed to conduct investigations on materials. Four autoclaves made of titanium are divided two by two in ovens. The autoclave can operate until 473 K and 20 MPa. An inert insert is placed in the cell to avoid the contact between the titanium and the fluid or the exposed materials. Temperature probes and pressure sensor enable the monitoring of experimental conditions.



Figure 2: Photograph of the corrosion pilot

In this work, two materials were studied: a carbon steel (DC01) and a stainless steel (304L). First, the microstructure of the materials were determined. Before exposition, material coupons were prepared according to the ASTM G1-03 [9]. Then, these coupons were placed into an autoclave containing brine at a given temperature and pressure. The coupons can be placed either in the gas phase or in the aqueous phase or at the gas/liquid interface. After different exposure times, the coupons were analysed.

First, a study of the weight loss allows the determination of the corrosion rate, which can be compared to the corrosion rate obtained by electrochemical measurements. The originality of this work is to associate surface analysis by XPS to the previous information. This technic enables the identification of corrosion products and their composition. By coupling the electrochemical and the surface analysis data, the comprehension of the corrosion mechanism and process can be improved. This leads to the determination of the most appropriate material from a technico-economic point of view: resistance to corrosive medium vs. cost of material. Further investigations could be led using inhibitors in the geothermal fluid in order to observe their impact on the reduction of the corrosion phenomena.

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