

Effects in the solubility of CaCO₃: Experimental study and model description

B. Coto^{a,*}, C. Martos^a, J.L. Peña^b, R. Rodríguez^a, G. Pastor^a

^a Department of Chemical and Energy Technology, ESCET, Universidad Rey Juan Carlos, C/Tulipán s/n, 28933 Móstoles, Madrid, Spain

^b Technology Center Repsol, 28933 Móstoles, Madrid, Spain

ARTICLE INFO

Article history:

Received 23 December 2011

Received in revised form 13 March 2012

Accepted 14 March 2012

Available online 23 March 2012

Keywords:

Calcium carbonate

Scale

Solubility

Electrolytes

ELEC-NRTL

ABSTRACT

Crude oil is usually co-produced with reservoir water, with increasing content in the production fluid along field life. Changes in temperature, pressure, and/or chemical composition may cause significant precipitation of inorganic salts (“scales”) during production. Therefore, the knowledge of the influence that different variables may have on salt solubility is critical to anticipate or identify potential flow assurance problems related to scales. The present work is specifically focused in the study of calcium carbonate precipitate formation as a main component of “scales”. Due to the number of variables involved in calcium carbonate precipitation (temperature, pressure, CO₂ partial pressure, other salt content) and the heterogeneity of reservoir conditions, there are serious limitations to perform a full experimental study covering all the possible precipitation scenarios. Solubility data presented in this work, both previously reported and experimentally determined, cover a wide range of experimental conditions.

A simulation model that allows quantitative predictions in different scenarios is an interesting tool. A versatile simulation algorithm was developed using ASPEN PLUS[®] 7.1 from Aspen Technology, Inc., that allows different experimental conditions and the quantification of the influence of temperature, pressure and pH in CaCO₃ solubility. This simulation scheme was applied to describe both literature and new experimental solubility data. Predicted results were in reasonable agreement with experimental information. The solubility of calcium carbonate decreases with temperature, increases with pressure and shows a maximum in presence of NaCl. The CO₂ partial pressure has strong effect because it is direct relation with solution pH that modify the amount of ionic species present in the aqueous solution, and hence increasing the solubility of calcium carbonate. Special attention was devoted to such pH effect but, in order to have a fully predictive model, no parameters fit was carried out. The main conclusion of this work is the suitable simulation scheme to describe and predict the solubility of calcium carbonate at different conditions.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The study of the effect of different variables on the solubility of calcium carbonate in aqueous solution is important to anticipate and/or mitigate potential flow assurance problems due to calcium carbonate scale formation and deposition during crude oil and associated water production. Reliable data of calcium carbonate solubility as a function of temperature, total and partial CO₂ pressure, pH and other variables are required to calibrate accurate simulation models capable to reproduce this complex equilibrium. The solubility of calcium carbonate in water has been published in different sources at room temperature and higher temperatures [1,2].

In geothermal fluids, significant amounts of carbon dioxide may exist at reservoir pressure and temperature conditions [2]. This

compound has a strong influence in the equilibrium of calcium carbonate solutions, and the salt solubility is strongly conditioned by the presence of this gas.

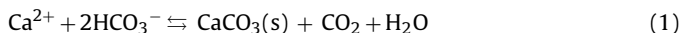
The complexity of the description of the solubility of calcium carbonate in water is due to the presence of simultaneous chemical equilibria of a high number of species (CO₃²⁻, HCO₃⁻, CO₂, etc.) involved in this process between solid, liquid and gas phases. Furthermore, if hydrocarbon phases are also present in reservoir conditions, CO₂ will also be present in the liquid hydrocarbon phase, adding another phase to the equilibria to be considered. According to these complex equilibria, the effect of both CO₂ partial pressure and pH can modify the distribution of different ionic species, affecting the deposition or the solubilization of the calcium carbonate [3].

The effect of pressure alone on the supersaturation of carbonate minerals in water solutions has usually minor significance. More important is the effect on the calcium carbonate solubility of carbon dioxide and the related chemical reactions that lead to the formation of CaCO₃ precipitate. Firstly, the

* Corresponding author. Tel.: +34 91 488 70 89; fax: +34 91 488 70 68.

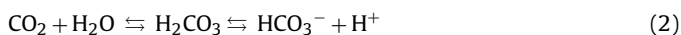
E-mail address: baudilio.coto@urjc.es (B. Coto).

precipitation of CaCO_3 is controlled by the following equilibrium (1):



Thus as pressure decreases, CO_2 is effectively lost from solution to the gas phase. Consequently, the driving force leading to the precipitation of CaCO_3 is increased according to the above equilibrium [4].

Secondly, the loss of CO_2 from the solution results in a reduction in the concentration of carbonic acid by the following chemical equilibrium (2), which consequently results in an increase in brine pH [2,3,5–7].



On the other hand, the high number of ionic species which appear in the solution of calcium carbonate makes the availability of the interaction parameter matrix of electrolyte thermodynamic model a priority for proper simulation models.

Formation waters contained in sedimentary rocks may have salinity values in a range of approximately five orders of magnitude [8], from dilute meteoric waters, with typical values of salinity below 10 g l^{-1} , to waters with salinity higher than 600 g l^{-1} . Considerable progress has been made in predicting the solubility of many common reservoir minerals, like calcium carbonate, in solutions with high ionic strength by applying the Pitzer virial-coefficient approach to estimate ion activities [9–12]. As well as Pitzer thermodynamic model, local composition models that express the excess Gibbs free energy due to short range intermolecular interactions such as the Wilson, NRTL and UNIQUAC models have been used as activity coefficient models in the prediction of salt precipitation [13–15].

As mentioned above, calcium carbonate is one of the main salts which may cause flow assurance problems, creating deposits on the production flowlines. In this case, the slow kinetic of the solubility process of calcium carbonate and the influence of pH, temperature, pressure, etc. [16] may change the equilibrium of this salt. As all the mentioned variables have a big effect on the precipitation of calcium carbonate, it is a challenge to carry out a full experimental study covering all the possible conditions and to develop simulation models able to describe all the experimental information.

The calculation of activity coefficients of salts in a saturated solution is the main problem in order to predict the scale precipitation. The Pitzer and The Electrolyte Non-Random Two Liquid (ELEC-NRTL) models are the most widely used models to estimate the activity coefficients for aqueous electrolyte systems [17].

The ELEC-NRTL model was originally proposed by Chen et al. [18,19], for aqueous electrolyte systems and later extended to mixed solvent electrolyte systems [5,20]. The ELEC-NRTL model is a versatile model for the calculation of activity coefficients that can be applied for all the concentration range using exclusively binary parameters, while Pitzer model is restricted to electrolyte concentration up to approximately 6 m.

Despite the limitations of the models (absence of binary interaction parameters of some electrolytes), their applicability to the calculation of the thermodynamic equilibrium of electrolyte solutions have been tested by many authors [5–7,10,11].

Due to the challenges and complexity of the calcium carbonate system, the present work is focused on the compilation of reliable experimental data to evaluate the solubility of calcium carbonate in aqueous solution in a wide range of operating conditions and the validation of a thermodynamic model for calcium carbonate solubility evaluation. The influence of parameters such as temperature, pressure, and presence of NaCl in the solution will be studied by a simulation model under ASPEN PLUS® v7.1 software. This study focuses in predicting realistic oilfield water systems, and therefore, the calcium carbonate solubility was evaluated at high values

of ionic strength using both experimental and theoretical procedures. No literature data were found at the same range of ionic strength values. The validation of this model was carried out with calcium carbonate solubility data already reported in the literature and experimental data obtained in the present work.

2. Experimental

Table 1 summarizes CaCO_3 solubility data reported in the literature by different authors [1,12,21–47] at different conditions of temperature, ionic strength, etc. The existing reported data are relatively scarce, and not all the experimental conditions of the described experiments were reported.

The solubility of calcite is highly influenced by the amount of carbonic acid present in the solution (CaCO_3 solubility increases with CO_2 concentration). In that case, calcite solubility studies can be divided into different groups according to the amount of carbon dioxide employed. Many studies are focused on calcite solubility in pure water, without the presence of CO_2 [21–25]. To achieve that purpose, all the CO_2 dissolved in the water is eliminated by using vigorous boiling.

On the other hand, other authors study the calcium carbonate solubility with dissolved CO_2 . For that purpose, pure CO_2 is bubbled into the solution keeping constant the amount of CO_2 , while the temperature and/or pressure are changed [15,26–37]. Many of these authors measured calcite solubility in CO_2 – H_2O mixtures (CO_2 concentration is lower than saturation value). Another studies used a gas phase constituted by carbon dioxide and N_2 or air in different proportions. We have used literature data with experimental conditions similar to our work.

The solubility of calcium carbonate was experimentally determined in aqueous solution at different ionic strengths and temperature. Pure calcium carbonate and sodium chloride reagent grade ACS, provided by SCHARLAB, were used. The solutions were prepared with deionized and ultrapure water (Milli Q).

The experimental system is a RADLEYS carousel with six hermetic closed spherical glass reactors (250 mL each one) that can be stabilized at the same conditions of pressure and temperature (temperature was controlled within $\pm 0.1^\circ\text{C}$). An excess of calcium carbonate in water or in a NaCl solution was stirred at 95°C and atmospheric pressure in each reactor until phase and chemical equilibria were reached (approximately 4 days) as denoted by conductivity, pH and calcium concentration values were analyzed along time and used as equilibria indicators. A continuous stirring of 650 rpm was maintained during all the experiment. Every 2 days (stabilization time) a small aliquot of supernatant liquid was removed ($\sim 1 \text{ mL}$), weighted and filtered through a $0.45 \mu\text{m}$ filter. The filter must be warmed previously at the experimental temperature to avoid any precipitation or solution of solid. Afterwards, the glass reactors temperature was decreased 10°C and the mentioned experimental procedure was repeated again until the temperature reached 25°C . In order to study the repeatability of the procedure, three different samples were taken at each temperature. The pH of the samples was measured directly from each reactor at every temperature with a CRISON MM40 multi-meter, calibrated previously with two buffer solution of pH 7 and 4.01.

The amount of calcium in dissolution was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a VARIAN Vista AX Axial CCD Simultaneous ICP-AES spectrometer. Calcium was analyzed at two wavelengths, 315.887 nm^{-1} and 317.933 nm^{-1} , and the average value was used. Calibration curve was obtained from Standard calcium solutions (concentration of 1000 mg/L , provided by SCHARLAB). Two different linear calibration curves were used for the ranges 0.25 – 5 mg/L and 10 – 80 mg/L .

Table 1
Literature calcium carbonate solubility data and experimental conditions.

Author	Year	Reference	T (°C)	P _{CO₂} (bar)	C _{NaCl} (mol dm ⁻³)
Segnit et al.	1962	1	75–200	40	0
Segnit et al.	1962	1	100	1–60	0
Miller	1952	27	0–105	1–100	0–0.5
Ellis	1963	31	100–300	2–150	0
Millero et al.	1984	12	25	–	0.1–6
Ponizovskii et al.	1980	41	25	0.02	–
Shtermina and Frolova	1945	43	–	–	–
Shtermina and Frolova	1957	42	–	–	–
Kaasa et al.	2005	44	–	–	–
Nagy	1988	45	–	–	–
Frear and Johnston	1929	36	25	1	–
Hastings et al.	1927	46	38	–	0.024–0.2
Yanatéva	1955a	28	0–55	1	–
MacDonald and North	1974	24	1–25	25.3–962.6	–
Weyl	1959	37	10–70	1	–
Mitchell	1923	26	25	1–24	–
Leather and Sen	1909	33	15–40	1	–
Johnston	1915	34	16	1	–
Lyashchenko and Churagulov	1981	25	25	1–1000	–
Kindyakov et al.	1958	22	25–75	1	–
Kendall	1912	21	25–100	1	–
Morey	1962	23	25–350	200	–
Yanatéva	1960	30	70	1	–
Ellis	1959a	29	98–302	1.9–142.3	–
Malinin	1963	32	100–300	2–150	–
Sharp and Kenedy	1965	38	197–300	20–1000	–
Nakayama	1968	47	25	0.01–1	–
Plummer et al.	1982	39	0.1–90	0.30–0.98	–
Wolf et al.	1989	40	10–60	0.01	0–6

3. Simulation model

The solubility equilibrium of calcium carbonate was simulated by means of flash separator (Fig. 1) using ASPEN PLUS®, which allows the effect of the different parameters in the CaCO₃ solubility to be evaluated.

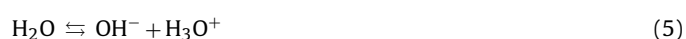
The flash separator is fed by two streams containing vapour and liquid phases. The inlet liquid stream (LIQ-IN) contains calcium carbonate saturated water (introduced in the system as CaCO₃ solid in excess plus water). The inlet vapour stream (V-IN) can be formed by carbon dioxide and/or air, and may be saturated with H₂O at the same pressure and temperature conditions of the first flash separator.

Pressure, temperature and stream compositions are set up in this first flash separator. At these conditions, the chemical is simulated and three phases equilibrium (liquid, gas and solid CaCO₃). The fluid outlet from the first separator is fed into the second flash, in which a different temperature is fixed at the same pressure conditions.

The pH of the outlet liquid stream fed into the second flash, is adjusted modifying the molar flow of a pure CO₂ stream until the experimental pH value is reached.

This scheme is repeated to reproduce experimental conditions from the highest temperature 95 °C to the lowest 25 °C. The streams at thermodynamic equilibrium that leave the last flash separator are constituted by the CO₂ and a small amount of H₂O (vapour phase) and by a two phases stream that contains all ionic species in solution (liquid phase) and the precipitated calcium carbonate (solid phase) at every pressure and temperature values.

The chemical reactions taken into account in the simulation process are the following:



The NRTL activity coefficient model modified for electrolytes systems (ELEC-NRTL) was used for the simulations. The calcium carbonate solubility was calculated as calcium molar concentration considering all the calcium species in aqueous solution once the pH was adjusted at each temperature step.

4. Results and discussion

Initially, the influence of temperature on the CaCO₃ solubility process was evaluated for both experimental and literature data, comparing the available CaCO₃ solubility provided by the simulation model. Table 2 shows the value of pH and calcium carbonate solubility in the different cases studied, the temperature range studied was between 25 and 95 °C at 1 bar of pressure and different concentrations of NaCl from 0 to 2.4 mol dm⁻³ were studied. The thermodynamic model was used to simulate the experimental data at the conditions described in Section 2 (different temperatures and atmospheric pressure). Fig. 2 illustrates this comparative study. As it is shown, the thermodynamic model simulates the experimental data of the calcium carbonate solubility in water accurately, the errors associated with the measure of calcium concentration was calculated by different repetitions of the same experiment in the same conditions, in Fig. 2 are plotting the different errors obtained in each point and as we can see in this figure the values of calcium carbonate solubility obtained in each point are very accurately with the thermodynamic model used. Fig. 3 shows the comparison between simulated calcium carbonate solubility (expressed as calcium molar concentration) with data reported in the literature [1,27,31]. In the simulation scheme, the temperature was varied from 10 to 170 °C at a fixed pressure of 40 bar of CO₂ by using ELEC-NRTL model. Strong temperature dependence for the CaCO₃ solubility was described by the model and, as it can be

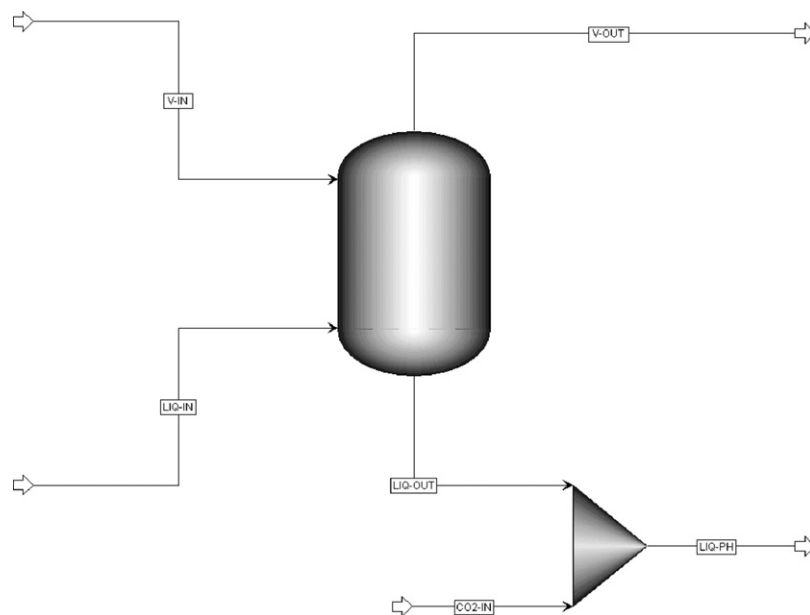


Fig. 1. ASPEN simulation model for the system. V-IN=inlet vapour stream; LIQ-IN=inlet calcium carbonate solution; V-OUT=outlet equilibrium vapour stream; LIQ-OUT=outlet equilibrium liquid stream (calcium carbonate solution); CO2-IN=inlet CO₂ support to fixed pH value; LIQ-PH=obtained calcium carbonate solution with pH adjusted to experimental values.

seen, these results are in reasonable agreement with those referenced in literature. After analyzing both figures (Figs. 2 and 3) it is remarkable that the solubility of this salt decreases with the temperature, and therefore, a decrease of this variable reduces the precipitation of calcium carbonate, as expected [14]. The effect of pressure in the CaCO₃ illustrated by these two figures shows that if the pressure increases the solubility of calcium carbonate increases too.

Fig. 4 depicts the influence of the partial pressure of CO₂ on the solubility process of calcium carbonate. This figure compares referenced data [1,27] at 100 °C and different pressures to the simulated values. As it is shown, the simulation of the process varying the pressure in the range of 1–70 bar at a fixed temperature of 100 °C yields an increase of the solubility curve of calcium carbonate in agreement to data referenced in the literature.

The variation in the CaCO₃ solubility with pressure can be explained by the simultaneous equilibriums involved in this process. As stated above, the presence CO₂ is of high importance as it modifies the amount of the species present in aqueous solution.

Thus, calcium carbonate is slightly soluble in pure water, but the solubility increases when carbon dioxide is present in the solution [3]. Therefore, higher partial CO₂ pressures make the amount of calcium in the solution increase [1].

Fig. 5 plots the simultaneous influence of the temperature and the pressure of CO₂ on the solubility of calcium carbonate values were obtained by simulation. The most important effect observed is the increase on calcium carbonate solubility in two orders of magnitude in presence of CO₂, as stated above. The effect of temperature on calcium carbonate solubility, seems to increase at higher partial pressure of CO₂, decreasing as temperature increases.

As it is mentioned in Section 1, the presence of carbon dioxide in the gas phase is associated in addition to changes in pH changes. Fig. 6 shows the relationship between CaCO₃ solubility and pH in the aqueous solution comparing both simulation and literature data reported by Nakayama [47] at a fixed temperature value of 25 °C at a fixed pressure of 1 bar. Aqueous solution pH is of a great importance as lower values of pH (high P_{CO₂}) modifies the amount of the species present in the aqueous solution (increasing the amount of

Table 2
Experimental calcium carbonate solubility data and experimental conditions determined in this work.

Experiment	T (°C)	P (bar)	C _{NaCl} (mol dm ⁻³)	pH ^a	C _{Ca²⁺} ^b × 10 ⁴ (mol dm ⁻³)
1	25	1	0.0	8.31	5.26 ± 0.65
2	35	1	0.0	8.34	4.53 ± 0.36
3	45	1	0.0	8.31	3.7 ± 0.43
4	55	1	0.0	8.34	3.34 ± 0.43
5	65	1	0.0	8.35	2.75 ± 0.22
6	75	1	0.0	8.33	2.39 ± 0.27
7	85	1	0.0	8.35	2.27 ± 0.27
8	95	1	0.0	8.34	1.83 ± 0.22
9	25	1	0.6	9.34	9.23 ± 0.37
10	25	1	1.2	9.41	11.01 ± 0.07
11	25	1	1.8	9.67	10.70 ± 0.30
12	25	1	2.4	9.95	10.10 ± 0.46
13	95	1	0.6	8.43	7.92 ± 0.40
14	95	1	1.2	8.54	9.11 ± 0.56
15	95	1	1.8	8.80	8.16 ± 0.33
16	95	1	2.4	9.00	7.40 ± 0.15

^a δ_{pH} = ±0.01. Calculated by repeating the experiment six times.

^b in the table. Calculated by repeating the experiment six times.

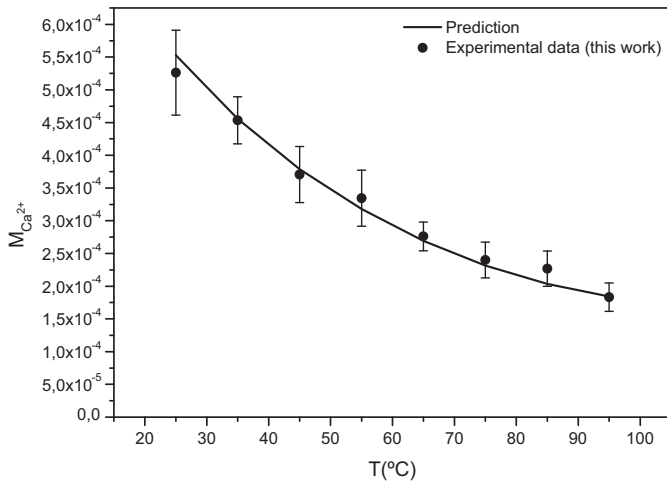


Fig. 2. Influence of the temperature on the CaCO₃ solubility (P=1 bar).

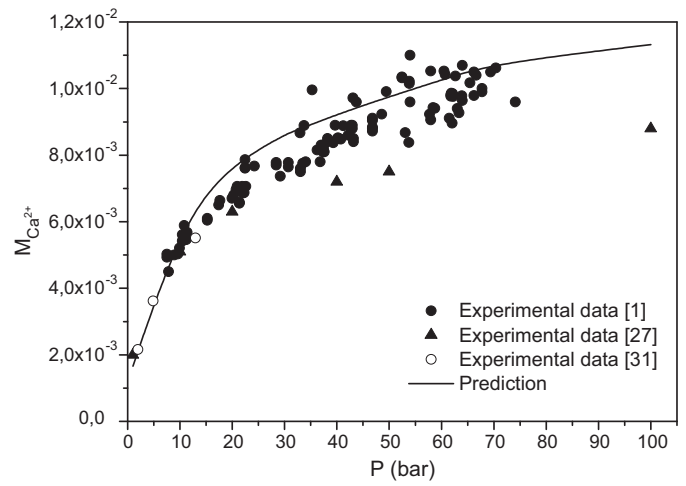


Fig. 4. Influence of the pressure on the CaCO₃ solubility (T=100 °C).

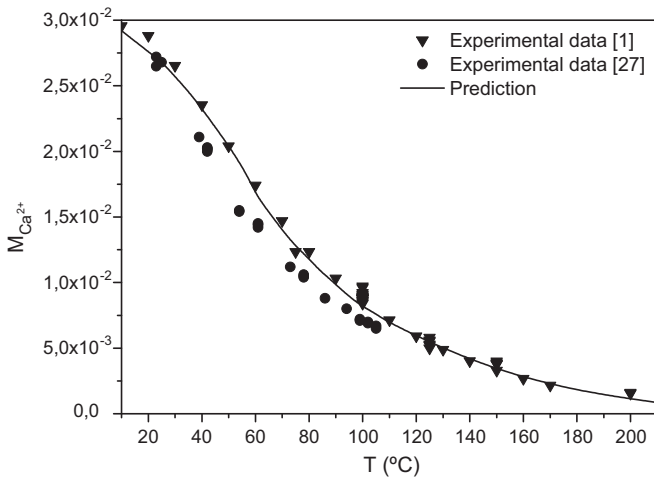


Fig. 3. Influence of the temperature on the CaCO₃ solubility (P=40 bar).

HCO₃⁻ and CO₃²⁻), causing the solubility of calcium carbonate to increase. The simulated data using ELEC-NRTL model are similar to the theoretical values reported by Nakayama [47]. These results of calcium concentration are obtained knowing CO₂ partial pressure and thermodynamic constants in the same conditions used in the ASPEN system. Both results emphasize the influence of pH (as a function of the amount of CO₂ in the system) in the chemical equilibria involved at the solubility process.

Increases of the solubility of a salt increases when other salt is present is a main topic in order to simulate real formation water systems, with significant amounts of Na⁺ and Cl⁻ ions. The influence of the presence of NaCl in the CaCO₃ solubility was studied in this work. Table 2 shows the value of pH and calcium carbonate solubility at different NaCl concentrations. Fig. 7 shows the variation of CaCO₃ solubility against the molar concentration of added NaCl at a pressure value of 1 bar and three different temperatures (T=25 and 95 °C) both experimental and simulated values are plotted. As it is shown, the thermodynamic model accurately reproduces experimental data when pH is fitted to experimental value. Moreover, analyzing Fig. 8 it can be seen that, as expected, solubility values are higher for the simulations performed with added NaCl. A maximum solubility value is obtained for an approximate NaCl

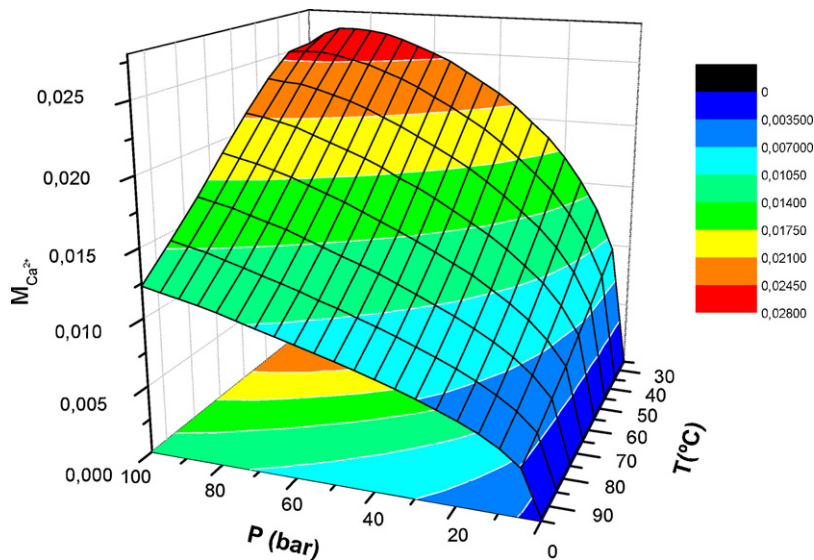


Fig. 5. Simultaneous influence of the pressure and the temperature on the CaCO₃ solubility.

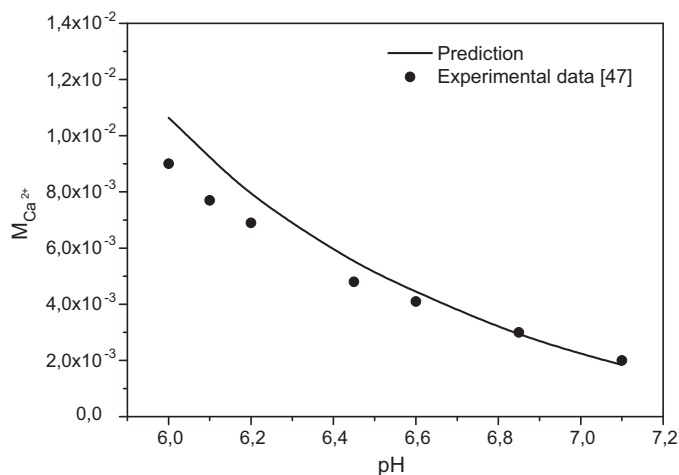


Fig. 6. Effect of the pH on the CaCO_3 solubility at 25°C and 1 bar air pressure.

concentration of 1.25 mol dm^{-3} in solution for all the temperatures. That NaCl concentration, at which solubility reaches the maximum value, is similar to the seawater salinity. Therefore, it is interesting to remark that the extraction of the crude oil with high salinity formation water is probably carried out at maximum CaCO_3 solubility conditions. The presence of maximum values for all the temperatures in Fig. 7 leads to the conclusion that no an increase of the solubility can be reached although higher amounts of NaCl are added to the solution.

Additionally, the thermodynamic model was used to predict the solubility results reported by Millero et al. [12] at different NaCl concentration at a fixed pressure of 1 bar as illustrated in Fig. 8 and so the comparison with Millero et al. [12] data could only be made to describe the ionic strength influence. After analyzing simulated and experimental results reported in this figure, no meaningful differences among these curves are shown at low concentration values, until 1 mol dm^{-3} of sodium chloride concentration, whereas at higher values of ionic strength (NaCl concentration) the simulation curve shows a deviation probably due to the difficulty of the ELEC-NRTL to reproduce high NaCl concentrations, close to the solubility limit.

When Figs. 2, 4 and 8 are considered together, important differences in Ca^{2+} concentration can be observed. Fig. 2 shows a calcium carbonate solubility value around $5 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C and 1 bar of air pressure whereas in Fig. 8 solubility is

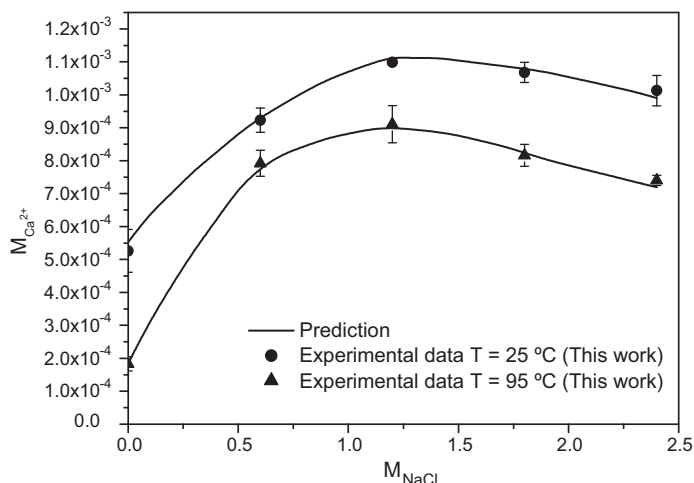


Fig. 7. Influence of the presence of NaCl on the CaCO_3 solubility at 1 bar air pressure.

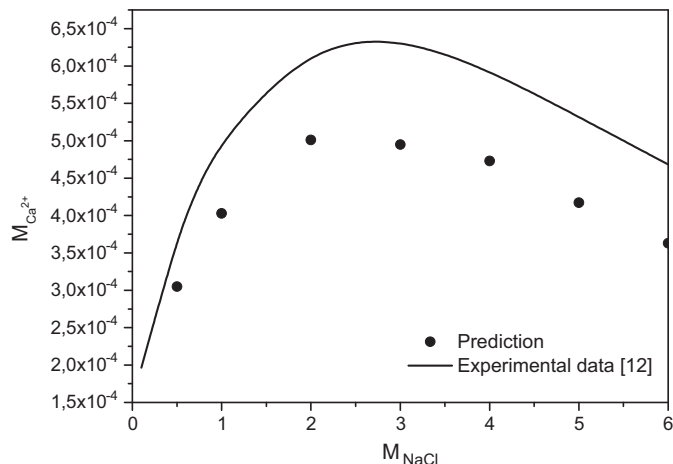


Fig. 8. Influence of the presence of NaCl on the CaCO_3 solubility at 25°C and 0.97 atm CO_2 pressure.

around $9 \times 10^{-3} \text{ mol dm}^{-3}$ at 25°C and 1 bar of CO_2 pressure when $M_{\text{NaCl}} = 0 \text{ mol dm}^{-3}$. On the other hand, Fig. 4 shows a value of solubility around $2 \times 10^{-3} \text{ mol dm}^{-3}$ at 100°C and 1 bar of CO_2 pressure. This different magnitude order in solubility value cannot be explained in terms of pressure or temperature changes. A significant difference is obtained by analyzing pH values in these three cases. For data plotted in Fig. 2, the involved pH was 8.33 determined experimentally and reproduced by simulation. However, for data plotted in Figs. 4 and 8, the involved pH were 5.48 and 6.07, respectively, both determined by simulation from the experimental conditions reported in literature. Therefore, the presence of CO_2 is a main variable because it modifies significantly the pH of the solution which has a strong effect on solubility value in agreement with that shown in Fig. 6.

As it has been demonstrated during the simulation study, this thermodynamic model maybe applied to real crude oil production schemes, being a useful tool to predict potential scaling problems. Consequently the tested model can be satisfactorily considered to describe the real CaCO_3 solubility chemistry and be used to evaluate conditions to avoid or minimize oil formation risk.

5. Conclusions

In the present work, a thermodynamic model under ASPEN PLUS simulation environment was considered to evaluate CaCO_3 solubility in water. ELEC-NRTL model and several ionic equilibria were considered. In this scheme a simple phase separator was used, being the system pressure is controlled by introducing a vapour phase stream where the amount of CO_2 can be modified. The influence of pressure, temperature, NaCl concentration and pH was studied for both literature and experimental data. The increase of solubility of CaCO_3 with the decrease of temperature, as well as the increase of pressure and increase of CO_2 partial pressure, are well described and in agreement with experimental values. Solubility shows a maximum against NaCl tested concentration for salinity values similar to that high salinity formation waters. The relationship between CO_2 partial pressure and pH is also described, leading to the expected decrease in solubility of calcium carbonate with increasing pH.

Simulation results are also in reasonable agreement with those reported in literature. However, the effect of NaCl is poorly predicted by this model providing higher solubility values than those reported by Millero et al. [12]. However, the main conclusion of this work is the suitable simulation scheme to describe and predict the solubility of calcium carbonate at different conditions.

The application of this model could be used to predict the amount of calcium carbonate deposited in equilibrium at any conditions of pressure, temperature, etc. in realistic conditions during crude oil production, and should be a valuable tool for flow assurance risk assessment studies to minimize scale formation.

Acknowledgment

The authors thank REPSOL S.A. for their financial support through the research project “Aseguramiento de flujo de crudos de petróleo: Estudio de la compatibilidad de aguas”.

References

- [1] E.R. Segnit, H.D. Holland, C.J. Biscardi, *Geochim. Cosmochim. Acta* 26 (1962) 1301–1331.
- [2] A. Satman, Z. Ugur, M. Onur, *Geothermics* 28 (1999) 425–444.
- [3] L. Lipus, D. Dobersek, *Chem. Eng. Sci.* 62 (2007) 2089–2095.
- [4] E. Mackay, *Chem. Eng. Res. Des.* 81 (2003) 326–332.
- [5] B. Mock, L. Evans, *Chem. Eng. Sci.* 32 (1986) 1655–1664.
- [6] D. Trendafelov, C. Christov, C. Balarew, A. Karapetkova, *Collect. Czech. Chem. C* 60 (1995) 2107–2111.
- [7] R. Rabindra, J. Gibbons, R. Williams, L. Godwin, G. Baker, *J. Chem. Thermodyn.* 16 (1984) 303–315.
- [8] J.S. Hanor, *Mar. Petrol. Geol.* 11 (1994) 31–45.
- [9] K.S. Pitzer, *J. Phys. Chem.* 77 (1973) 268–277.
- [10] K.S. Pitzer, G. Mayorga, *J. Solution Chem.* 77 (1973) 2300–2308.
- [11] K.S. Pitzer, G. Mayorga, *J. Solution Chem.* 3 (1974) 539–546.
- [12] F.J. Millero, P.J. Milne, V.L. Thurmond, *Geochim. Cosmochim. Acta* 48 (1984) 1141–1143.
- [13] H. Kuramochi, M. Osako, A. Kida, K. Nishimura, K. Kawamoto, Y. Asakuma, K. Fukui, K. Maeda, *Ind. Eng. Chem. Res.* 44 (2005) 3289–3297.
- [14] A. Villafañila, K. Thomsen, E. Stenby, *Geothermics* 35 (2006) 239–284.
- [15] J.C. Raposo, J. Sanz, G. Borge, M.A. Olazabal, J.M. Madariaga, *Fluid Phase Equilib.* 155 (1999) 1–19.
- [16] J. Moghadasi, H. Mueller-Steinhagen, M. Jamialahmadi, A. Sharif, *J. Petrol. Sci. Eng.* 43 (2004) 163–181.
- [17] B. Messnaoui, T. Bounahmidi, *Fluid Phase Equilib.* 244 (2006) 117–127.
- [18] C. Chen, L. Evans, *AIChE J.* 32 (1986) 444–454.
- [19] C. Chen, H. Britt, J. Boston, L. Evans, *AIChE J.* 28 (1982) 588–596.
- [20] B. Mock, L. Evans, C. Chen, *Summer Computer Simulation Conference*, 1984, p. 558.
- [21] J. Kendall, *Philos. Mag. Ser. 23* (1912) 958–976.
- [22] P.S. Kindyakov, A.V. Khokhlova, L.L. Lapchinskaya, *Tr. Mosk. Inst. Tonkoi Tekhnol.* 7 (1958) 32–44.
- [23] G.W. Morey, *Am. Mineral.* 47 (1962) 1456–1460.
- [24] R.W. MacDonald, N.A. North, *Can. J. Chem.* 52 (1974) 3181–3186.
- [25] A.K. Lyashchenko, B.R. Churagulov, *Russ. J. Inorg. Chem.* 26 (1981) 642–644.
- [26] A.E. Mitchell, *J. Chem. Soc.* 123 (1923) 1691–1692.
- [27] J.P. Miller, *Am. J. Sci.* 250 (1952) 161–203.
- [28] O.K. Yanatéva, *Akad. Nauk SSSR* 26 (1955) 266–269.
- [29] A.J. Ellis, *Am. J. Sci.* 257 (1959) 354–365.
- [30] O.K. Yanatéva, *Russ. J. Inorg. Chem.* 5 (1960) 1247–1250.
- [31] A.J. Ellis, *Am. J. Sci.* 261 (1963) 259–267.
- [32] S.D. Malinin, *Geokhimiia* 650 (1963) 650–667, 631–645.
- [33] J.W. Leather, J.N. Sen, *Mem. Dept. Agric. India* 1 (1909) 117–131.
- [34] J. Johnston, *J. Am. Chem. Soc.* 37 (1915) 2001–2020.
- [35] R.C. Wells, *Washington Acad. Sci.* 5 (1915) 617–622.
- [36] G.L. Frear, J. Johnston, *J. Am. Chem. Soc.* 51 (1929) 2082–2093.
- [37] P.K. Weyl, *Geochim. Cosmochim. Acta* 17 (1959) 214–225.
- [38] W.E. Sharp, G.C. Kennedy, *J. Geol.* 60 (1965) 391–403.
- [39] L. Plummer, E. Busenberg, *Geochim. Cosmochim. Acta* 46 (1982) 1011–1040.
- [40] M. Wolf, O. Breitkopf, R. Puk, *Chem. Geol.* 76 (1989) 291–301.
- [41] A.A. Ponzovskii, I.N. Lepeshkov, V.T. Orlova, *Russ. J. Inorg. Chem.* 25 (1980) 1716–1720.
- [42] E.B. Shtermina, E.V. Frolova, *Russ. J. Inorg. Chem.* 2 (1957).
- [43] E.B. Shtermina, E.V. Frolova, *Doklady Akad. Nauk SSSR* 50 (1945) 261–264.
- [44] B. Kaasa, K. Sandengen, T. Ostvold, *SPE 95075* (2005) 1–13.
- [45] K.L. Nagy, PhD thesis, Texas A&M University, 1988.
- [46] A.B. Hastings, C.D. Murray Jr., J. Sendroy, *J. Biol. Chem.* 71 (1927) 723–781.
- [47] F.S. Nakayama, *Soil Sci.* 106 (1968) 429–434.