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Effect of limestone and buffer solution in the aqueous speciation and pH of brines for CO₂ sequestration

Patricia Córdoba, Leïla Cherqaoui, Susana Garcia*, M. Mercedes Maroto-Valer

*Centre for Innovation in Carbon Capture and Storage (CICCS), School of Engineering and Physical Sciences, Heriot-Watt University,
Edinburgh EH14 4AS, United Kingdom*

Abstract

Oil-field brines, a by-product of oil and natural gas extraction whose fate is mainly disposal, is gaining attention for the storage of CO₂ into geologically stable mineral carbonates. The suitable pH range for the formation of carbonates is 7.8 or higher, where CO₃²⁻ dominates. Therefore, to boost the precipitation of mineral carbonates by reaction between brine and CO₂, the pH of the brine must be modified before any brine-CO₂ interaction takes place. In this work, pH stability studies were conducted to study how synthetic brines respond in the presence of a natural limestone host rock or a tris buffer solution in both closed and open atmospheres and to evaluate the efficiency of both buffers at increasing brine pH. An aqueous and solid speciation model was used to investigate the influence of the buffer used in the aqueous and solid speciation of two synthetic brines. pH stability studies identified that both buffers can enhance brine pH, being tris buffer the one with the strongest buffer efficiency. Both XRD and geochemical modelling results suggest the suitability of brines containing SO₄²⁻ and the use of both host rock and tris buffer, respectively, to enhance oil-field brines pH for mineral carbonates precipitation.

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* Corresponding author. Tel.: +44 (0)131 451 8083.
E-mail address: s.garcia@hw.ac.uk

1. Introduction

Oil-field brines, a by-product of oil and natural gas extraction whose fate is mainly disposal [1], is gaining attention for the storage of CO₂ into geologically stable mineral carbonates. Brines have significant concentrations of Ca, Mg and Fe, which react with CO₂ to produce CaCO_{3(s)}, MgCO_{3(s)}, Fe₂CO_{3(s)} and other products under favourable conditions. However, most oil-field brines are generally acidic in nature with a typical pH ranging from 3 to 5 [2, 3], so that carbonates will not form in this pH range. The suitable pH range for formation of carbonates is 7.8 or higher [3], where CO₃²⁻ dominates. Therefore, to boost the precipitation of mineral carbonates by reaction between brine and CO₂, the pH of the brine must be modified before brine-CO₂ interaction [2].

Biocatalysts, buffer solutions [4, 5], and strong bases such as KOH have been studied as buffer alternatives to enhance brines initial pH. However, a factor that should be considered as the first step to boost the precipitation of mineral carbonates by the increase of the pH in oil-field brines is the speciation of Fe [6] and the occurrence of SO₄²⁻. A significant concentration of SO₄²⁻ in brines could reduce the reactivity of Ca, Mg and Fe for CO₂ and/or decrease limestone dissolution rate because of coating of CaSO₄ [7]. With this in mind, pH stability studies were conducted to 1) study how two synthetic brines with different composition, with and without SO₄²⁻, respond in the presence of either a natural limestone host rock or a buffer solution (tris buffer (C₄H₁₁NO₃)) in both closed and open atmospheres before any brine-CO₂ interaction, 2) evaluate the efficiency of both buffers at increasing brine pH, and to 3) determine the suitability of oil-field brines containing SO₄²⁻ for CO₂ sequestration via stable mineral carbonate formation.

2. Methodology

Two different synthetic brines, namely B1 and B2, were prepared as an analogue to an oil-field brine (OH-2) which comes from a natural gas well in Youngstown, Ohio [8, 9]. Owing to the complex composition of oil-field brines, only major ions were considered to prepare the two synthetic brines, including Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺/Fe²⁺, Sr²⁺, Ba²⁺ Cl⁻ and SO₄²⁻. The main difference between B1 and B2 composition is the absence of SO₄²⁻ ions in the B1 aqueous phase.

A natural limestone, as host rock, and tris buffer (C₄H₁₁NO₃), as additive, were selected as buffer systems because of their efficiency to boost brine pH from their initial pH values to an upper limit under which carbonate minerals may precipitate (pH ≥ 7.8). The starting adjusted pH target value was pre-established according to the pH value reached after addition of the host rock to both B1 (8.5 pH) and B2 (6.9 pH) brines, respectively.

pH stability studies were conducted with the limestone host rock and tris buffer using both B1 and B2 at ambient temperature and pressure in both closed and open atmospheres to assess their buffering ability. Closed atmosphere studies would indicate primary influence of the buffer in changing brine pH, while the open atmosphere studies are necessary to provide insight on how atmospheric CO₂ can affect the brine pH. A total of four experiments, two sets of B1 and B2, were conducted for the limestone rock-brine and tris buffer-brine studies. B1 and B2 pH was then measured every 5 to 10 min for the first 2h and every 30 min for the next 8 h. In the following days, the pH of both B1 and B2 was measured twice a day in closed atmosphere. When the brine pH was stable around ±0.2 continuously for 3 days, the stability study in a closed atmosphere was then completed. Beakers were then allowed to remain open to the atmosphere for 3 days in order to assess how both B1 and B2 brines naturally respond to the CO₂ in the atmosphere.

Brines aqueous phases were analysed before and after experiments by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with an X-SERIES II device from Thermo Quantitative. Analyses were performed with an external calibration using an external standard of similar matrix to the samples. The internal correction was carried out by means of an internal standard (In 10 ppb). 20 mL of each B1 and B2 were vacuum filtered using a cellulose nitrate membrane filters (0.45 μm pore size) and acidified with HNO₃ (1% v/v) to prevent

oxidation of ions and stabilise the metal concentration. Brine solid phases were analysed by X-Ray powder Diffraction (XRD) to determine the mineralogical composition of any products precipitated after host rock and buffer addition. Analyses were carried out by using a HILTONBROOKS diffractometer with monochromatic Cu $K\alpha_{1,2}$ radiation operated at 40KV and 20mA, from 4-60° 2 θ , at a step size of 0.05°, and scan rate of 3s/step.

Theoretical calculations were computed with the PHREEQC code (version 2.0) to calculate the 1) ion activities and distribution of ionic species of both synthetic brines and 2) saturation indexes (SI) with respect to mineral and solid phases after the addition of limestone host rock and tris buffer, respectively. The modelling calculations were conducted by using experimental conditions as well as the chemical composition and pH values of the two brines as input data. The theoretical results from the model were then compared to experimentally derived results on the same system.

3. Results and discussion

3.1. pH studies

The initial, adjusted and final pH values of the tested brines are given in Table 1. B1 duplicates, namely B1a and B1b, show an initial pH of 6.55 and 6.59, respectively, while B2a and B2b show an initial pH of 1.95 and 1.94, respectively. The difference between the B1 and B2 pH is produced as a consequence of the NaHSO₄ dissolution in the B2 aqueous phase.

Table 1. pH values of brines and selected experimental parameters in the pH stability studies.

Brine type	Initial pH	Added host rock (mmoles)	Adjusted pH	Final pH
B1A	6.55	10.10	8.41	7.61
B1B	6.59	10.10	8.50	7.61
B2A	1.95	10.10	6.91	7.61
B2B	1.94	10.10	6.91	7.62
Brine type	Initial pH	Added Tris buffer (mmoles)	Adjusted pH	Final pH
B1A	6.56	0.01	8.57	7.14
B1B	6.58	0.01	8.61	7.20
B2A	2.12	0.82	6.88	6.75
B2B	2.12	0.82	6.89	6.80

3.1.1 Limestone host rock experiments

The results of pH studies for B1 and B2 over a period of 800 h (33 days) are shown in Figure 1a and 1b, respectively. The pH of B1a and B1b increases from the initial values ~6.6 to around 8.4 due to the addition of the limestone host rock, after which it decreases progressively and fluctuates over the first 150 h (± 0.2 pH). In the open atmosphere, B1a and B1b pHs remain stable at 7.6 (± 0.2 pH) until the end of the experiment (Figure 1a). The pH of B2a and B2b, containing SO₄²⁻, increase sharply after limestone rock addition, reaching a stable pH of 7.6 in the closed atmosphere. In the open atmosphere, the B2a and B2b pH maintain a stable pH of 7.7 until the end of the experiment. The different trend between the B1 and B2 pH is due to both the different limestone dissolution rate and equilibrium conditions between B1 and B2 aqueous phases. The extremely acidic conditions of B2 aqueous phase (pH 1.95), as a consequence of the dissolution of NaHSO₄, lead to a high limestone dissolution rate in B2.

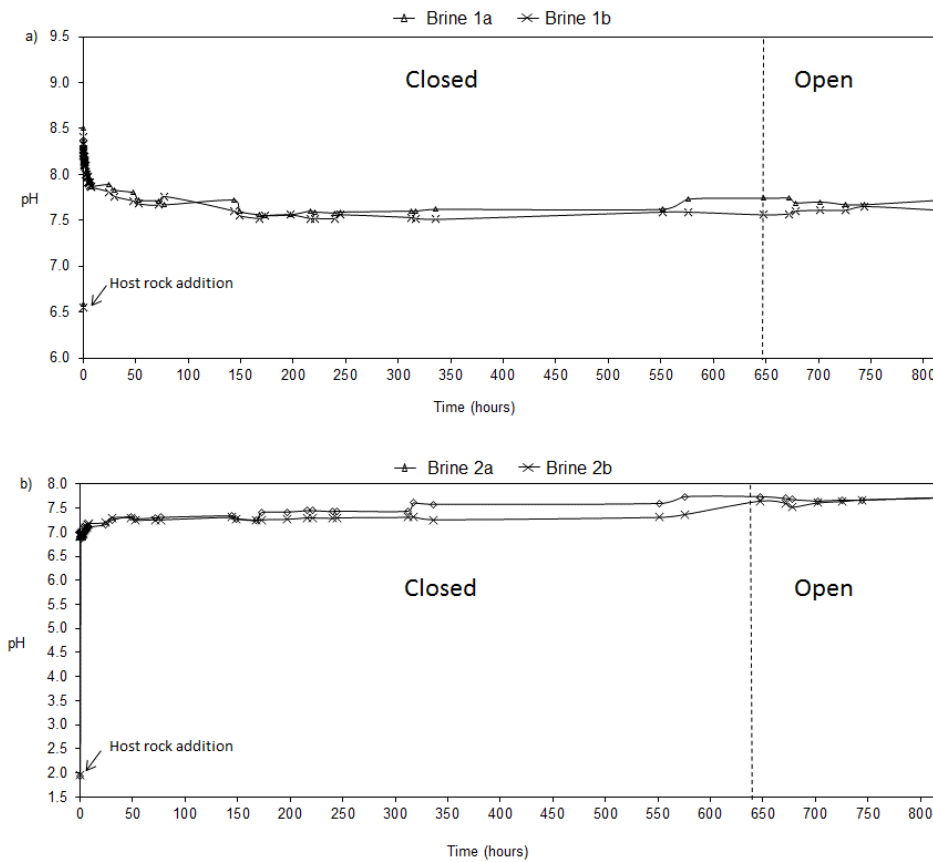


Fig. 1. a) B1a and B1b pH over time after host rock addition; b) B2a and B2b over time after host rock addition.

The composition of the oil-field brine (OH-2) and synthetic brines in each set of experiments is shown in Table 2. Results reveal a good agreement between the concentration of major elements in both B1 and B2 (before experiments) with the target values.

Table 2. Composition of Oil-field (OH-2) and B1 and B2 brines.

	Brines-host rock							
	OH-2 (target)		Before experiments		After experiments			
	B1	B2	B1	B2	B1a	B1b	B2a	B2b
Ca ²⁺	639	639	679	672	682	737	828	869
Na ⁺	8963	8963	8563	8995	8344	8268	8777	8065
Mg ²⁺	69	69	73	77	85	90	94	96
K ⁺	227	227	277	271	277	298	293	301
Sr ²⁺	59	59	57	59	45	49	45	49
SO ₄ ²⁻	775	-	863	-	-	-	793	840
Cl ⁻	14695	14695	14561	14161	13961	14061	14921	14967

As expected, after the host rock addition, both B1 and B2 aqueous phases have a higher concentration of Ca^{2+} because of the CaCO_3 dissolution. The higher concentration of Ca in B2 versus that in B1 is due to a higher dissolution rate of CaCO_3 because of the B2 acidic pH (1.95). The higher concentration of Mg in B1 and B2 after host rock addition is probably due to a partial dissolution of Mg-containing impurities (e.g. $\text{CaMg}(\text{CO}_3)_2$) from the limestone host rock, while the lower concentration of Na and Cl in B1 and B2 is most likely to be the result of NaCl precipitation. XRD analyses from host rock experiments, not shown here, revealed that CaCO_3 is the main crystalline phase detected in B1 and B2 as it is the main component of the host rock. The non-identification of SO_4 -solid species (CaSO_4 , MgSO_4 , FeSO_4 , MnSO_4 , etc) in B2 by XRD, would indicate, in first instance, the suitability of brines containing SO_4^{2-} and the use of this host rock to enhance oil-field brines pH. A significant concentration of SO_4^{2-} in brines could reduce the reactivity of Ca, Mg and Fe for CO_2 by forming the above mentioned SO_4 -species and/or decrease the host rock dissolution rate by coating of CaSO_4 particles on its surface [7].

3.1.2. Tris buffer experiments

The results of pH studies for B1 and B2 over a period of 408 h (17 days) are shown in Figure 2a and 2b, respectively. The evolution of the pH of the B1 against time shows that the pH of B1a and B1b increase sharply to around 8.6 after the addition of the tris buffer, showing fluctuation periods after 24, 72, 168, and 264 h. The B1a and B1b pH reach a relative stability at around 7.9 and 7.7, respectively, in the closed system. In the open atmosphere, both B1a and B1b pH decrease progressively and reach the stability at 7.1. Results show that B2 experiences a sharp drop of the pH over the first 24 h and fluctuate after 72 h. The pH of the B2 duplicates, B2a and B2b, containing SO_4^{2-} also increases after the addition of the tris buffer in the closed atmosphere. In the open atmosphere, B2a and B2b pH remain stable at 6.8 till the end of the experiment (Figure 2b).

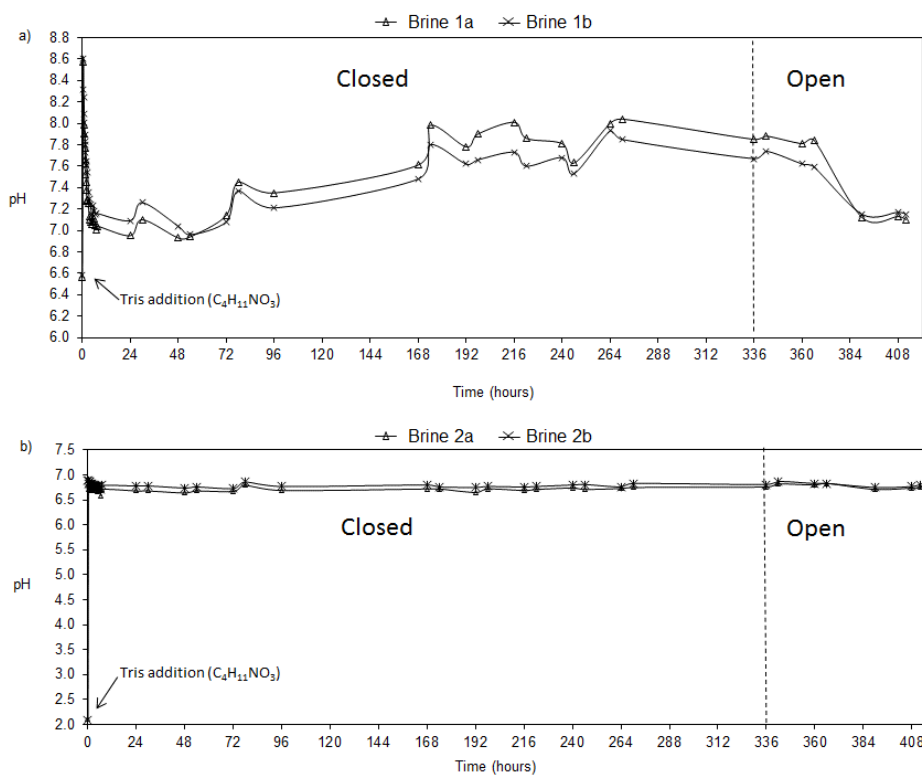


Fig. 2. a) B1a and B1b pH over time after tris buffer addition; b) B2a and B2b over time after tris buffer addition.

There are also differences in the pH between B1 and B2 in terms of stabilization period. The longer stabilization period of the pH for B1 compared with that of the B2 may be due to 1) precipitation of mineral and/or solid phases which may result in variations of the B1 pH, especially over the open atmosphere period, and to the 2) lower tris buffer volume added in B1 (0.02mL for B1 and 2.73mL for B2), accounting for a low buffer efficiency in the B1 aqueous phase.

Table 3. Composition of Oil-field (OH-2) and B1 and B2 brines.

	Brines-tris buffer							
	OH-2 (target)		Before experiments		After experiments			
	B1	B2	B1	B2	B1a	B1b	B2a	B2b
Ca ²⁺	639	639	655	700	590	609	587	594
Na ⁺	8963	8963	8063	8333	8051	8044	8301	8352
Mg ²⁺	69	69	71	80	61	62	63	63
K ⁺	227	227	267	287	238	232	219	219
Sr ²⁺	59	59	58	63	50	53	52	52
SO ₄ ²⁻	-	775	-	910	-	-	758	777
Cl ⁻	14695	14695	14021	14328	14058	14006	14347	14395

After the tris buffer addition (Table 3), the concentration of most elements in both brines is similar with the exception of Na⁺ and Cl⁻, which is the result of NaCl precipitation in B1 and B2 as revealed by XRD. The non-identification of SO₄-solid species (CaSO₄, MgSO₄, FeSO₄, MnSO₄, etc) in B2 by XRD, would indicate, in first instance, the suitability of brines containing SO₄²⁻ and the use of tris buffer to enhance oil-field brines pH. A significant concentration of SO₄²⁻ in brines could reduce the reactivity of Ca, Mg and Fe for CO₂ by forming the above mentioned SO₄-species.

3.2. Geochemical modelling: aqueous and solid speciation of brines

According to the geochemical modelling, prior to the host rock and tris buffer addition, the B1 and B2 aqueous phases are undersaturated (SI = IAP/K < 0) with respect to all mineral and solid phases, and Cl⁻ (as free ion), Ca²⁺ and Na⁺ (as free cations), and NaCl are the aqueous complexes with the highest activities at the initial pH of 6.5 (B1) and 1.9 (B2), respectively. NaSO₄⁻(aq), CaSO₄⁰(aq), KSO₄⁻(aq), MgSO₄⁰(aq), and SrSO₄⁰(aq) are also present, with lower activities, in the B2 aqueous phase.

When modelling host rock addition to B1, the geochemical modelling predicts the occurrence of NaCO₃⁻(aq), MgCO₃⁰(aq), NaHCO₃⁰(aq), SrCO₃⁰(aq), CaHCO₃⁺(aq), and MgHCO₃⁺(aq) aqueous complexes and the oversaturation of the B1 aqueous phase with respect to Mg species such as Mg₅(CO₃)₄(OH)₂·4H₂O (SI of 2.95), and Sr species such as SrCO₃ (3.53). This suggests that the higher concentration of Mg in the B1 aqueous phase after host rock addition could be the result of a partial dissolution of Mg₅(CO₃)₄(OH)₂·4H₂O (SI of 2.95) from the host rock.

When modelling host rock addition to B2, the geochemical modelling predicts that CaCl⁺(aq) followed by CaSO₄⁰(aq) have the highest activity of Ca in the B2 aqueous phase. However, CaHCO₃⁺(aq) and CaCO₃⁰(aq), NaHCO₃⁰(aq), NaCO₃⁻(aq), and MgHCO₃⁺(aq) aqueous complexes increase their activity when adding CaCO₃ (≈ 7 mmol CaCO₃), which is the result of the host rock dissolution and formation of carbonate and bicarbonate aqueous complexes. No solid phases are predicted to be saturated in the B2 aqueous phase when adding the same amount of CaCO₃ as the one used in the experiment.

The geochemical modelling predicts the occurrence of CaNO₃⁺, SrNO₃⁺, CaNO₃⁺, HNO₃, HNO₂, and NO₂⁻ in

both B1 and B2 with tris buffer addition. Nevertheless, the addition of the tris buffer to the B1 aqueous phase does not alter the stability and speciation of the initial aqueous complexes; Cl^- (as free ion), Ca^{2+} and Na^+ (as free cations), and NaCl are the aqueous complexes with the highest activities in both B1 and B2 after tris buffer addition. Tris buffer also promotes the oversaturation ($\text{SI} = \text{IAP}/\text{K} > 0$) of Mg, Ca, and Sr-carbonate species in the B1 and B2 aqueous phases. This confirms that tris buffer has a buffering capacity between pH 7.0 and 9.2, which is in line with the suitable pH range for carbonates formation (7.8).

4. Conclusions

The results reveal that both, a limestone host rock and a tris buffer, can enhance the pH of two different oil-field brines, B1 and B2, where the only difference between them is the presence (B2) or absence (B1) of sulfate ions. A natural limestone host rock was shown to increase both B1 and B2 pH to nearly 7.6, whereas tris buffer resulted in a B1 and B2 pH of 7.2 and 6.8, respectively. However, in terms of efficiency, tris buffer shows the strongest buffer ability and the smallest volume added.

Brines containing SO_4^{2-} and the use of both host rock and tris buffer, respectively, are suitable to enhance oil-field brines pH to required values for the precipitation of mineral carbonates by brine- CO_2 reactions. No minerals or solid phases containing SO_4^{2-} are predicted to be oversaturated in the B2 aqueous phase after adding either host rock or tris buffer. This finding would be quite important as a significant concentration of SO_4^{2-} in brines could reduce the reactivity of Ca, Mg and Fe for CO_2 and /or decrease the host rock dissolution rate by coating of CaSO_4 particles on its surface.

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