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Article

Microcalorimetric Study of Carbonating Produced Water as a Promising CO_2 Storage and Enhanced Oil Recovery Method

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Abstract: Carbonated produced water injection (CPWI) might be considered an efficient alternative to handle the largest waste stream while enhancing the oil recovery and storing carbon dioxide (CO_2) underground. This study was an attempt to get a deeper understanding of the oil recovery process through synergy between spontaneous imbibition and isothermal titration calorimetry (ITC) experiments. The results from the spontaneous imbibition experiments showed 7% to 11% additional oil recovery in comparison with plain produced water. Rock–fluid and fluid–fluid interactions, evaluated by isothermal titration calorimetry (ITC) experiments, confirmed that the CPW interactions with oil+EFB+chalk and oil+EFB systems are much more exothermic than those with plain PW in those systems. The synergy between spontaneous imbibition and ITC experiments provides an improved understanding of carbonated water injection in carbonate reservoirs.

Keywords: enhanced oil recovery (EOR); CO_2; carbonated produced water injection; rock–fluid; fluid–fluid; interactions

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1. Introduction

Awareness of climate change and its negative effects has increased since the global concentration of carbon dioxide (CO_2) in the atmosphere has been rising significantly [1]. CO_2 emission is an inevitable side-effect of burning fossil fuels, which play an important role in the global energy mix of the 20th century [2]. In order to achieve substantial reductions in greenhouse gas emissions while enabling sustainable energy production, anthropogenic CO_2 must be captured, transported, and stored subsequently in geological formations such as deep saline aquifers, coal beds, and depleted oil and gas reservoirs [3–5]. Among those options, depleted oil and gas reservoirs are the best options because of (1) the presence of a wealth of data since the formations have been extensively evaluated, (2) the existence of infrastructure, and (3) revenue from the incremental oil recovery due to CO_2 injection [6]. CO_2 flooding has been widely and successfully used in many oil fields. It contributes to over 5% of the total United States' oil production. Various CO_2 techniques (continuous/slug injection, simultaneous water and gas injection-SWAG, and the water alternating gas process—WAG) have been developed to recover additional oil from depleted reservoirs while at the same time storing large quantities of CO_2 underground [7,8]. Carbonated water injection (CWI) is gaining rapid attention because it is a viable option that can be used onshore and offshore. This technique was conceptualized in the 1930s, but more serious research started in the 1970s [9]. Basically, in CWI, CO_2 is dissolved in brine prior to its injection into a depleted oil reservoir. CWI is an excellent technique for both EOR and CO_2 sequestration because the solubility of CO_2 in water is higher than that of other gases (e.g., nitrogen and light hydrocarbon gases). The main advantages of CWI are (1) better mobility ratio of CO_2 brine than those of other pure gases, (2) higher density of CO_2 brine than that of pure brine, which reduces the risk of CO_2 leaking, (3) improvement in the sweep efficiency because it suppresses the fingering problem of the pure CO_2 injection, (4) reduction in viscosity as CO_2 moves from the brine to the oil phase, (5) improvement in the rock wettability towards more water-wet conditions due to fluid-rock interactions, (6) production of oil globules trapped in the pore space due to crude oil swelling, (7) delay in water or gas breakthrough [6,10]. Chen et al. [11] found that carbonated water increases the hydrophilicity due to reductions in the contact angles. Those authors developed a geochemical model that couples CO_2 dissolution, mineral dissolution, and oil and calcite surface chemistry. According to those authors, the model gives information of the mechanistic CO_2-induced wettability shift, and it can be used in larger reservoir simulators.

Microcalorimetry is a direct appraisal of the heat absorbed or released during a binding interaction between molecules. The measured heat can be used to obtain enthalpy (ΔH) changes which are associated with the adhesion of different fluids onto a rock surface [12–14]. One type of microcalorimetric technique is isothermal titration calorimetry (ITC). It allows one to accurately determine thermodynamic parameters, such as entropy (ΔS), Gibbs free energy (ΔG), affinity constant (Kd), and binding stoichiometry (n) [12]. The popularity of ITC is because of its robustness, speed, and small sample consumption [15]. The degree of accuracy of this technique is higher than those of alternatives (e.g., Van 't Hoff equation) because the enthalpy is determined from measurements [16]. In our previous works, microcalorimetry was proven to be useful for the understanding of complex rock–fluid and fluid–fluid interactions for both enhanced oil recovery and geothermal energy production [2,13,16–18].

This study aimed to gain insights into the complex rock–fluid and fluid–fluid interactions that take place during carbonated produced water injection (CPWI) through spontaneous imbibition and microcalorimetry experiments. The synergy between those experiments showed which part of the rock–fluid and fluid–fluid system is responsible for the enhanced oil recovery observed during the spontaneous imbibition experiments. To the best of our knowledge, this had not done before, since the rock–fluid and fluid–fluid interactions have not been thoroughly investigated from a calorimetric point of view. The present work fills this gap, clarifying the CW EOR system. Moreover, it provides relevant insights into the usage of produced water for carbonated water injection. The possibility of using produced water for CO_2-EOR and CO_2 storage in carbonates is appealing, since this fluid is considered to be the most problematic source of waste in the oil and gas industry.

2. Materials and Methods

2.1. Fluids

Synthetic Ekofisk formation brine (EFB) was prepared by mixing reagent grade salts with distilled water (DW). EFB contains 67.3 g/L NaCl, 14.69 g/L $CaCl_2$, 4.45 g/L $MgCl_2$, 2.27 g/L $SrCl_2$, 0.55 g/L KCl, 0.45 g/L $BaCl_2$ and 0.33 g/L $NaHCO_3$. Halfdan produced water (PW) was obtained from a Danish North Sea well and consists of a mixture of brine, precipitates, crude oil, and possibly other chemicals. The ionic composition of PW was investigated by inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer instruments) and an 800 series ion chromatography (IC) instrument from Metrohm. Table 1 presents the composition of PW.

Table 1. Ionic composition of the Halfdan produced water (PW).

Ions	Na^+	Ca^{2+}	Mg^{2+}	K^+	Sr^{2+}	SO_4^{2-}	Cl^-	Br^-	F^-
Concentration (g/L)	29.2	0.98	0.42	0.51	0.14	0.15	49.0	0.16	0.02

Crude oil from a North Sea carbonate reservoir was used in the experiments presented in this study [16]. Impurities (solid particles and water) were removed by centrifuging the crude oil at 3800 rpm for at least one hour. A Tiamo 2.4, Metrohm autotitrator unit was used to measure the acid (AN) and basic (BN) numbers. The oil density and viscosity were measured with a DMA 35 Anton Paar density meter and a PVS rheometer from Brookfield, respectively. Table 2 displays the crude oil properties.

Table 2. The crude oil's properties.

AN (mg KOH)/g	BN (mg KOH)/g	Viscosity mPa.s	Density g/cm^3
0.52	1.60	11.94	0.86

2.2. Rock Material

Austin chalk was used for spontaneous imbibition and isothermal titration calorimetry (ITC) experiments. A part of the rock material was crushed and grounded with a ball mill to obtain particles with a size of <100 µm. Those particles were used for the ITC experiments and elemental composition testing by a Rigaku supermini 200 X-ray fluorescence (XRF) machine. Table 3 displays the results from the XRF analysis [17].

Table 3. X-ray fluorescence (XRF) analysis of Austin chalk.

	Compound									
	CaO	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SrO**	**Fe_2O_3**	**K_2O**	**SO_3**	**Cl**
%	95.90	1.20	0.40	1.60	0.20	0.10	0.30	0.10	0.13	0.02

The Austin cores were washed gently with tap water to remove loose particles before the spontaneous imbibition experiments. Dry weights and dimensions of those core plugs were measured using Mitutoyo's Absolute Digimatic Caliper after being dried in a heating cabinet at 65 °C for 2 weeks. Thereafter, the cores were air evacuated and saturated with Ekofisk formation brine (EFB) for 24 h and weighed again. The initial porosity and air permeability of the Austin cores were determined by an AP-608 Automated Permeameter–Porosimeter from Coretest systems. The Austin chalk core properties and an overview of the workflow used in this study are presented in Table 4.

Table 4. Core data for Austin chalk and an overview of experiments.

Core id.	l [cm]	d [cm]	PV [mL]	ϕ %	k_w [mD]	Aging Method	Aging Time [h]
AC-5	7.64	3.79	24.13	28.00	31.92	Static	1000
AC-6	7.62	3.77	24.86	29.22	30.41	Static	1000
AC-8	7.63	3.74	21.14	25.16	19.36	Static	1000

2.3. Aging Procedures

Fully brine-saturated Austin chalk core plugs (AC-5, AC-6, and AC-8) were put inside a desiccator with silica gel to achieve 15% connate water (Sw_i). Then, crude oil was injected in both directions at a low flow rate (0.1 mL/min) into a core plug placed in a Hassler-type core holder that was kept in an oven at 50 °C. Note that the confining pressure was 10 bars above the injection pressure, and the back pressure was set to 10 bars. In total, 2 pore volumes (PV) were injected in each direction to achieve uniform initial water saturation. After crude oil saturation, the core plug was wrapped with Teflon to ensure a uniform wettability distribution [19]. Thereafter, the core plug was submerged in aging cells with filtered crude oil and stored at no-flow conditions for 1000 h at 50 °C. Wrapping the cores with teflon avoids the precipitation of heavy fractions in the crude oil on the core boundary (circumference), which causes the imbibition to only occur in the interior of the core plug and not in the outermost layer of the cores. In a previous work [18], it was shown that limestone cores aged in no-flow conditions (statically) only imbibed oil spontaneously when the inner part was in direct contact with the wetting fluid. Therefore, it was mentioned that all faces open (AFO) boundary conditions could not capture the tendency towards weakly oil-wet conditions in the interior of the core samples in statically-aged core plugs, and special precautions should be taken.

2.4. Spontaneous Imbibition Experiments

An aged core plug was placed inside a high-temperature Amott–Harvey imbibition cell that was modified by adding a relief valve and an injection valve. The carbonated Halfdan produced water (CPW) was injected into the cell up to the level of the slim graduated cylinder. As there was a pressure build up due to free CO_2; the injection was stopped for 2 h to allow the free CO_2 to re-dissolve in the produced water before the injection was resumed. This filling-up process was done 3 times with a waiting time of 2 h. When the injection was completed, the injection valve was closed to ensure that system was completely sealed and CO_2 did not escape from the Amott cell. The crude oil production was recorded every 2–3 h until it reached a plateau.

A schematic illustration of the setup used for the injection of carbonated water into the Amott cell is presented in Figure 1. As observed, a close system was used for the experiments. In order to determine a comparable amount of CO_2, the solubility of that gas in distilled water was determined through a solubility vs. temperature plot from Engineering ToolBox [20]. The reading value was 0.75 g CO_2/kg water, corresponding to a temperature of 50 °C.

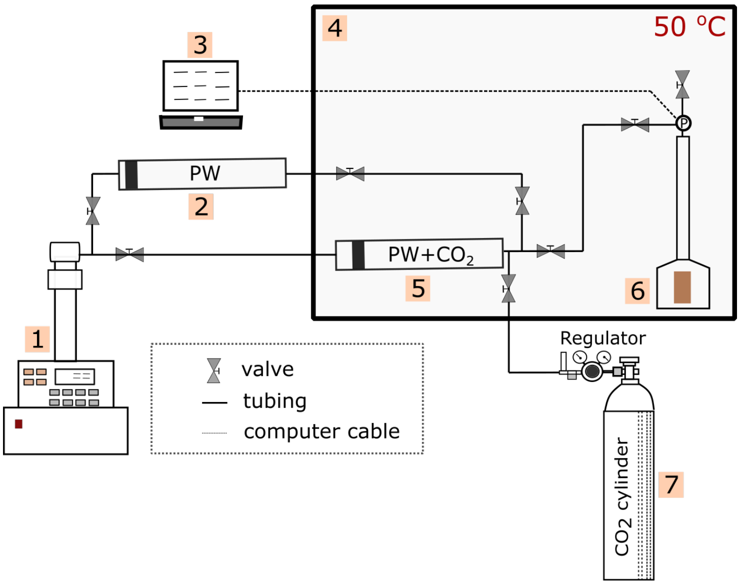

Figure 1. Experimental set-up for spontaneous imbibition with carbonated water (produced water with CO_2: 1—Teledyne ISCO pump, 2—piston#2, 3—computer, 4—oven, 5—piston#3, 6—Amott cell with core plug, 7—CO_2 cylinder.

The solubility value was converted to its equivalents in saline water using Equation (1) proposed by Kilybay et al. [21]. In this equation, R_{sb} is the CO_2 solubility in saline water (g/kg), R_{sw} is the CO_2 solubility in water (g/kg), C is the total dissolved solids in the water given as weight percentage of salts (kg) to the weight of water (% kg/kg), and T is temperature (°F).

$$log\left(\frac{R_{sb}}{R_{sw}}\right) = -0.028 * C * T^{-0.12} \tag{1}$$

Thereafter, the solubility was converted to a mole basis, and the number of CO_2 moles required to saturate 400 mL Halfdan produced water (PW) was determined. The calculations indicate that 0.00529 mol is needed for each imbibition experiment. The pressure required to inject those 0.00529 mols of CO_2 in piston#3 was calculated by the ideal gas law. The results show that 2.9 bar was needed to saturate the 400 mL PW that was injected from piston#2 to piston#3 (see Figure 1). Once PW has been injected, piston#3 should be left inside the oven kept at 50 °C in no-flow conditions for 24 h. According to Kilybay et al. [21], this should be done to ensure the complete miscibility of CO_2 in the fluid.

2.5. Microcalorimetry Procedures

A multichannel TAM IV microcalorimetric system from TA Instruments was used to characterize the injection of carbonated Halfdan produced water (CPW) into the same rock+fluid system (chalk+EFB+crude oil). One-hundred milligrams of Austin chalk was placed in an ampule. Then, 200 µL of EFB and 200 µL of crude oil were added to the rock particles to resemble an oil reservoir [13,16–18]. The ampule was lowered into the TA microcalorimeter until it reached its final measuring position. Thereafter, CPW was added to the chalk+EFB+oil system. Note that the interval between injections was 600 s. The interaction between CPW and EFB+crude oil was also determined similarly but without the rock particles.

Baseline experiments were also carried out using a similar procedure. The experiments consisted in adding separately PW into chalk+EFB+crude oil and EFB+crude oil systems.

The ITC experiments were analyzed by $NanoAnalyze^{TM}$ software from TA Instruments.

3. Results and Discussion

3.1. Spontaneous Imbibition

The imbibition fluid for AC-5 was Halfdan produced water, whereas it was carbonated Halfdan produced water for AC-6 and AC-8. Figure 2 shows the spontaneous oil imbibition for Austin core plugs after being aged statically for 1000 h. The time from the core plugs being submerged in the imbibition fluid (produced water or carbonated produced water) until they started expelling oil was less than 1 h. This short induction time shows the potential of produced water to enhance oil recovery. As shown in Figure 2, carbonated produced water gives higher oil recovery than plain produced water.

An increment of between 7% and 11% was obtained when the imbibition fluid was saturated with CO_2 in comparison to Halfdan produced water (PW). Sohrabi et al. [3] also obtained higher oil recovery with carbonated water injection (CWI) than with plain water injection. The brine was made of 0.8 wt% sodium chloride (NaCl) and 0.2 wt% calcium chloride hexahydrate ($CaCl_2 \cdot 6\,H_2O$). Those authors concluded that the potential of CWI in both secondary and tertiary recovery modes is significant. This is because 19% PV incremental oil recovery in comparison to plain WI was obtained in secondary mode, whereas 9.2% PV incremental oil was produced in tertiary mode. Seyyedi et al. [22] also observed a significant additional oil recovery by using carbonated synthetic seawater. Additional production of 10% of the original oil in place (OOIP) was obtained in a heterogeneous sandstone core plug. Consequently, the performance of a carbonated fluid is not impacted by heterogeneities in the rock. Zou et al. [23] obtained significant additional production in tight oil reservoirs compared to conventional waterflooding in both secondary and tertiary injection modes by 20.3% and 11.3%, respectively. The proposed mechanisms in the literature for the better performance of carbonated water injection are (1) oil swelling and subsequent viscosity reduction due to CO_2 dissolution in the oil phase, (2) improvement in sweep efficiency due to reconnection of isolated droplets and fluid flow diversion, and (3) wettability alteration [9].

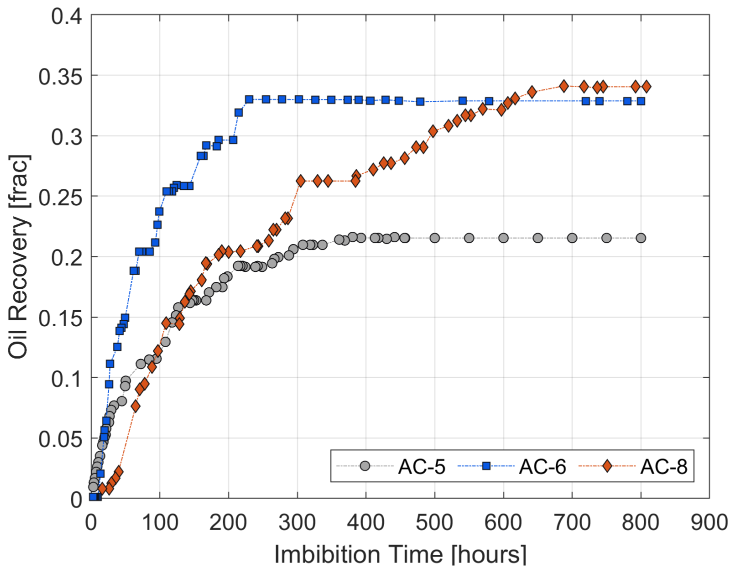

Figure 2. Spontaneous oil imbibition characteristics for core plugs exposed to formation water (AC-5) and carbonated formation water (AC-6, AC-8).

The ionic compositions of the brines before and after the spontaneous imbibition experiments, with a focus on the alkaline earth metal group, are presented in Table 5. As observed, Ca^{2+} and $SO_4{}^{2-}$ concentrations increased after the spontaneous imbibition with CPW in AC-6 and AC-8 core plugs. This could indicate that carbonic acid dissolved minerals containing those elements (e.g., calcite and anhydrite). In Table 5, slight changes in the Mg^{2+} and Sr^{2+} concentrations are shown, which could be related to the minor presence of those minerals. Riazi [24] presented scanning electron microscopy (SEM) pictures of a sandstone core before and after being in contact with carbonated water for 2 weeks at a pressure of 2000 psi and a temperature of 38 °C. The SEM images show that effectively the sandstone was corroded by bicarbonate due to prolonged exposure to the carbonated water.

Table 5. Ionic composition measured as g/L of all the fluids used in the spontaneous imbibition experiments for AC5 (plain PW), AC6(CPW), and AC8 (CPW).

Ions	Before Experiment	After Experiment		
		AC-5 (Plain PW)	**AC-6 (CPW)**	**AC-8 (CPW)**
Ca^{+2}	0.98	0.97	1.24	1.30
Mg^{+2}	0.42	0.43	0.41	0.49
Sr^{+2}	0.14	0.15	0.15	0.18
$SO_4{}^{-2}$	0.15	0.18	0.85	0.90

3.2. Rock–Fluid and Fluid–Fluid Interactions

The interaction between carbonated produced water (CPW) and the oil+EFB+chalk system was measured to gain further insights into the mechanisms responsible for the higher imbibition rate reported previously. The raw heat signal registered in the TAM IV microcalorimeter when CPW was added directly into the chalk+EFB+oil system is presented in Figure 3. The heat flow signal indicates an exothermic event according to the data collection of the ITC equipment. In other words, when CPW contacted the chalk+EFB+oil system, an exothermic process took place inside the microcalorimeter's reaction vessel. It can be noticed in Figure 3 that the heights of the peaks are larger at the beginning of the process than at the end. This is be because the CO_2 transfer to the crude oil was higher at the beginning than at the end due to more and more saturation of the oil, EFB, chalk system with CO_2. Note that each peak observed in the figure represents a single addition of 9.947 µL into the chalk+EFB+oil system.

CPW was injected into the crude oil+EFB system to determine the physicochemical interactions that occur at the oil–water interface. The heat flow obtained for the injection of CPW into crude oil+EFB (fluid–fluid interaction) is presented in Figure 3. As observed, the peaks are much higher than the ones observed in Figure 3. This could indicate that the exothermic process that occurs when CPW is injected into an oil reservoir is driven by the fluid–fluid interactions and the dissolution of the chalk with carbonic acid is entropy driven.

Baseline ITC experiments were also performed to distinguish the impacts of CO_2 in the rock–fluid and fluid–fluid interactions. In this case, Halfdan produced water (PW) was injected into either crude oil+EFB+chalk or crude oil+EFB systems. The thermogram of the interaction between PW and those systems is presented in Figure 3. As observed, no major changes were registered when PW was added to those systems. In other words, PW slightly interacts with the rock but not with the in situ crude oil. Those results show that effectively, crude oil was being diffused from CPW to the crude oil phase, giving a higher oil recovery.

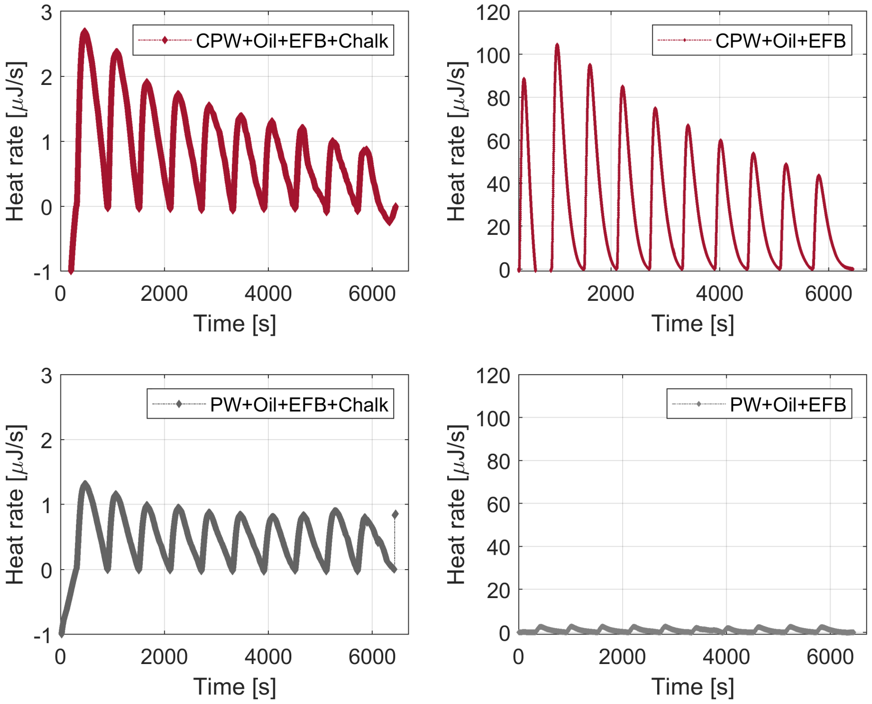

Figure 3. Heat rate versus time for carbonated produced water and produced water titrated into the system of oil, Ekofisk brine and chalk

The integration of the heat rate observed in Figure 3 over the baseline (time) gives the heat developed by each injection of 9.947 μL of CPW or PW into the rock–fluid (chalk+EFB+oil) or fluid–fluid (oil+EFB) system. Table 6 presents the results from the integration of the area between peaks and the baseline.

Table 6. Heat values for rock–fluid and fluid–fluid interactions.

	CPW System (mJ)		**Heat PW System (mJ)**	
Injection	**Oil+EFB+Chalk**	**Oil+EFB**	**Oil+EFB+Chalk**	**Oil+EFB**
1	−0.98	−16.35	−0.47	−0.62
2	−0.85	−23.86	−0.38	−0.59
3	−0.64	−22.43	−0.32	−0.57
4	−0.59	−19.89	−0.30	−0.59
5	−0.55	−17.91	−0.28	−0.58
6	−0.44	−16.10	−0.28	−0.62
7	−0.42	−13.98	−0.26	−0.36
8	−0.31	−12.57	−0.26	−0.54
9	−0.30	−11.36	−0.31	−0.60
10	−0.18	−10.86	−0.29	−0.53

The results presented in Table 6 clearly show that the heat responses for injecting CPW into chalk+EFB+oil and oil+EFB systems are much higher than those for injecting PW into the same systems. In this sense, the total interaction heat for the injection into the chalk+EFB+oil system was −6.02 mJ, whereas the injection of PW into the same rock–fluid system was −3.16 mJ. Thus, the overall reaction was more exothermic for CPW than PW.

When carbonated water makes contact with the in situ oil, CO_2 migrates from the water phase into the oil phase because it has a higher solubility in hydrocarbons [25]. Seyyedi et al. [4] conducted a series of high pressure and high-temperature direct visualizations (micromodel) and compositional variation (PVT) experiments. Those experiments were done to get insights into the complex fluid–fluid interactions and compositional changes that occur during carbonated water injection (CWI). According to these authors, a one-way CO_2 mass transfer from the injection fluid into crude oil takes place during CWI. This mass transfer results in an oil viscosity reduction that leads to a color change (oil became lighter) due to rapid nucleation of CO_2 within the oil phase. Seyyedi and coauthors [4] also found that the in situ oil composition does not change during carbonated water injection. Only after extensive pore volumes of CW was the in situ crude oil composition changed due to the small extraction of light components into a condensate phase. Those results are in accordance with the microcalorimetry findings reported in this work, in which CO_2 dissolved in the carbonated fluid was mainly interacting with the in situ crude oil. As presented in Table 6, the total interaction heat for CPW into oil+EFB was −165.32 mJ. The interaction between PW and the reservoir fluids was negligible because the PW did not contain CO_2.

A graphical representation of the microcalorimetric system and the one-way CO_2 mass transfer into the in situ crude oil can be found in Figure 4. The consequence of that mass transfer is the formation of a new gaseous phase formed inside the oil phase that leads to crude oil swelling.

The combination of rock–fluid and fluid–fluid interactions could explain the enhanced oil recovery observed when carbonated produced water was used as an imbibition fluid. It is believed that both rock–fluid and fluid–fluid interactions are responsible for the observed oil recovery. The rock–fluid interactions are related to a wettability alteration from oil-wet to water-wet conditions, rock dissolution, and opening of new paths [26,27]. On the other hand, the fluid–fluid interactions can be associated with the mass transfer of CO_2 into the crude oil phase, leading to a better sweep efficiency due to swelling and improved mobility (viscosity reduction) of the crude oil.

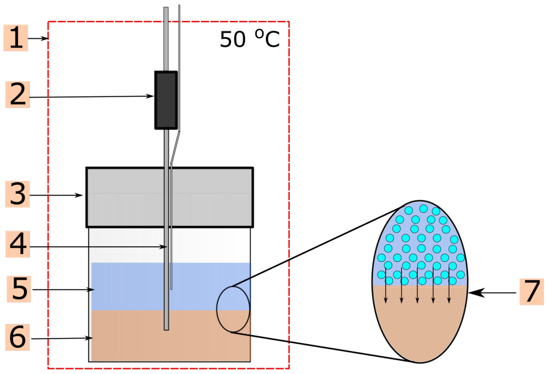

Figure 4. Graphical representation of the mass transfer happening during carbonated produced water injection and microcalorimeter description. 1—TAM IV microcalorimeter at 50 °C, 2—titration ampule, 3—reaction vessel, 4—titration shaft, 5—carbonated produced water, 6—crude oil and 7—CO_2 transfer.

The implication of both rock–fluid and fluid–fluid interactions is that CO_2 in the injection fluid (CPW) could be potentially stored in geological formations while recovering crude oil. Several studies in the literature [3,6,25,28] have reported this secondary benefit. Kechut et al. [28] showed that a high percentage of the total CO_2 volume (45–51%) is stored at the end of the secondary and tertiary carbonated waterfloods. According to those authors, the high solubility of CO_2 in the water phase increases the storing capacity in CWI and reduces the risk of buoyancy-driven leakage through micro-pores of the caprock.

4. Conclusions

- Carbonated produced water (CPW) injection increases the oil recovery by 7–11% in comparison to plain produced water (PW).
- The inorganic content (IC) showed that CO_2 dissolved in the production water caused rock dissolution, which was confirmed by an increase in the calcium concentration from 0.87 g/L before the spontaneous imbibition experiment to 1.2 after the experiment.
- The rock–fluid experiments indicate that CPW is more reactive than PW. The obtained heat for the interaction between CPW and chalk+EFB+oil was double the that for the interaction between PW and chalk+EFB+oil.
- The fluid–fluid experiments show that when CPW makes contact with the reservoir fluids (oil+EFB), CO_2 reacts strongly with the reservoir fluids. This effect was not observed for PW.
- Produced water with CO_2 is a promising fluid not only for enhanced oil recovery (EOR) purposes, but also for CO_2 sequestration and storage in oil reservoirs.

Author Contributions: J.E.C.: Conceptualization, Investigation, Methodology, Software, Validation, Visualization, Writing—Original Draft. Y.K.: Investigation, Methodology, Experimental Work. I.A.A.: Investigation, Methodology, Experimental Work. E.G.S.: Conceptualization, Validation, Experimental Work, Writing—Review and Editing. All authors have read and agreed to the published version of the manuscript.

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