

## Carbon dioxide hydrate formation in pure water and highly saline water

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**Abstract.** In this study, the hydrate kinetics for CO<sub>2</sub> gas was assessed in treating highly saline water at 3 MPa and 275.15 K to acquire perception towards water recovery and uptake of gas for desalination purpose. The experimentation was performed using a stainless-steel reactor by implementing isochoric (constant cooling) technique in treating highly saline water and related with the deionized water system. The study discloses that CO<sub>2</sub> hydrate forms quicker in deionised water at 75 mins achieving uptake of CO<sub>2</sub> gas as 0.0575 mol/mol with a recovery of 65.7% as opposed to 83.5 mins and uptake of gas of 0.0505 mol/mol and water recovery of 45.5% in 2.8wt% saline water sample. Hence it is evident that the existence of salts slightly inhibits the formation of hydrate but still produces a higher percentage of water recovery compared to conventional technologies. The results from this study are useful for the design of the efficient reactor for hydrate desalination.

### Introduction

The term "produced water" in the oil and gas segment refers to the water that is mixed with the oil throughout the extraction method and is highly saline than seawater. It is one of the major watercourses of effluent produced in the oil and gas industries, with an estimated global production in 2009 of >70 billion barrels per year, of which 21 billion barrels were generated in the US alone [1]. Produced water makes up the majority of the waste stream in production of oil and gas activities at offshore, accounting for 80% of the residues and wastes generated during the natural gas production and highly saline compared to seawater. Additionally, the quantity of produced water generated upsurges as the well's span upsurges, the production of oil drops [2]. With only 2% of fossil fuel output, the volume of water produced might reach 98% in nearly exhausted fields [3]. The water to oil ratio in the course of oil production is roughly 3:1 [4].

Produced water is a complex combination of inorganics (trace metals, salts, suspended particles), radioactive materials and organics (distributed and dissolved hydrocarbons, organic acids), as well as, frequently, residual chemical additives (corrosion inhibitors and scale inhibitors) that were added during the production of hydrocarbon. Prior to being released to the marine

environment, these compounds must be handled since they may have varied degrees of impact on the receiving environment. The availability of technology, cost, and local regulatory requirements all influence how produced water is treated. Produced water management is becoming increasingly difficult as the industry attempts to recover production from mature fields and develop new fields in difficult terrain due to high water cut, the existence of emulsion, and a considerable volume of contaminants like mercury (Hg), sand, and hydrogen sulphide. Due to these difficulties, the sector must investigate new or improved practical solutions for the management disposal and treatment of produced water that are more cost-effective and sustainable.

To eliminate the dissolved solids from the highly saline water, oil and gas producers have used membrane techniques, electric separation, distillation and treatment with chemicals [4-6]. Though these techniques are good enough to treat produced water but challenged with limitations like high energy requirement, large sludge generation, scaling and fouling issues. Hence there is a need to look into alternate desalination technologies like application of gas hydrate technology. The key benefits of this technology are that it theoretically requires less energy than previous methods[7] and that it has a low propensity to damage pipelines since it functions at low temperatures above the water freezing point. Gas hydrate desalination of seawater was initiated in the 1940s and acquired significant recognition from the 1960s to the present [8]. Owing to the structure of hydrates (water + guest component), salts and other pollutants of saline water can be removed during the formation of hydrate. Salt are removed from the hydrate structure owing to the cage size, varies between 0.395 to 0.571 nm [9-10]. After the hydrate has formed, it is dissociated to produce treated or pure water[8] [11-14]. The three structure types that make up hydrates' primary structures are sI, sII, and sH [15-16]. Some of the biggest issues of hydrate-based desalination are include the slow formation kinetics of hydrate, reuse of guest molecule, and hydrate-highly saline water separation. There is substantial literature available regarding the feasibility of this technology by using different hydrate formers like refrigerants and hydrocarbons[17-21]. But the various hydrate formers used for desalination purposes in literature are not biodegradable and either form a suspension leading to difficulty in the separation of hydrate and residual, hydrate former is insoluble in water and some of the hydrate formers damage the ozone layer. Hence it is desired to look into suitable guest molecules for hydrate-based desalination purpose that can enhance moles consumption and recovery of water.

In this paper the kinetics and use of hydrate-based desalination (HBD) in place of conventional techniques like distillation and reverse osmosis systems have been discussed. This study examines to contribute insights on the possible application of gas hydrates in desalination with respect to the effect of salts in treating produced water, by using CO<sub>2</sub> guest gas. The kinetic evaluation of moles of gas consumed uptake of gas and water recovery produced in treating highly saline water and comparatively assessed with the pure water system. The findings of the study provide insights into CO<sub>2</sub> hydrate formation and mechanism in presence of salts which are valuable to possibly treat saline water by producing a higher yield of treated water with CO<sub>2</sub> hydrates.

### **Methodology**

The system considered in this study produced water sample of 2.8 wt%. procured from West Patricia, offshore of Sarawak region at a latitude of 3°32'22.1"N and a longitude of 112°48'38.6". The composition of the highly saline-produced water sample is represented in Table 1. The guest component selected for the hydrate-based desalination is CO<sub>2</sub> to signify utilization of CO<sub>2</sub> in gas hydrate applications miscibility with water and ability to form hydrate at lower pressures compared to methane.

Table 1: Characterization of produced water sample

Materials Used	Supplier	Purity	Initial Ion concentration ( $C_{A_0}$ , g/l)					
			Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Salts	Merck	99.99%	7.858	0.277	0.744	0.293	13.61501	1.955
Gases								
Carbon dioxide (CO <sub>2</sub> )	Gas Walker Sdn Bhd	Assay ≥ 99.995%	-					
Ultrapure water	University Teknologi PETRONAS	18.2MΩ-cm	-					

In this work, the CO<sub>2</sub> hydrate kinetic experiments were measured using (99.9% pure CO<sub>2</sub>) to treat highly saline synthetic produced water. The illustrative drawing of the hydrate desalination reactor is represented in figure1 [11] The reactor is designated to function under high-pressure conditions (10MPa) and has a volume capacity of 2600 ml. In the experimental approach, the pressure and temperature discrepancies inside the reactor were supervised by means of three thermocouples ( reactor, chiller, and water bath) and two pressure sensors( gas inlet and reactor pressure). The hydrate reactor is submerged in the water bath. The system temperature is controlled by the water bath which is in turn linked to a chiller. Throughout the experimentation approach, the pressure and temperature variations of the reactor were logged via a data acquisition system. To execute each experiment, the reactor was initially fed with the synthetic highly saline water sample of 500ml volume through a high suction pump into the reactor. CO<sub>2</sub> gas is then pressurized to the experimental conditions of 3.0 MPa at 283.15 K. When the reactor was stable at the initial settings (3.0 MPa & 283.15 K), the experimentation was initiated by lowering the temperature from 283.15 K to the experimental condition of 275.15 °K to start hydrate formation. CO<sub>2</sub> hydrate formation was observed by a fast drop in the reactor pressure followed by a concurrent rise in the temperature owing to its exothermic nature. The hydrate formation was examined to be complete when the temperature and pressure in the reactor were steady. Then the residual saline water is emptied and the formed hydrates were washed with wash water to remove any salts occluded on their surface. The wash water is further drained out. The reactor is depressurized to dissociate the hydrate. The treated water is further collected and further analyzed for its initial final concentrations.

The CO<sub>2</sub> hydrate formation induction time ( $t_i$ ) was measured using the subsequent Eq. 1

$$t_i = t_s - t_h \quad (1)$$

where  $t_s$  and  $t_h$  represent the time period at the start of the experimentation and the instant when hydrates formed, respectively.

The quantity of CO<sub>2</sub> hydrates formed was assessed by measuring the gas uptake at the initial point (time  $t=0$ ) and any time  $t$  using Eq. 2

$$(\Delta n_H) = \left(\frac{PV}{zRT}\right)_0 - \left(\frac{PV}{zRT}\right)_t \quad (2)$$

where  $\Delta n_H$  is the CO<sub>2</sub> gas uptake and V is volume, P is pressure, T is temperature, and R signifies the molar gas constant, z is the compressibility factor evaluated using Pitzer's correlations.

Water recovery is calculated based on the volume of hydrate produced to the initial volume of feed input by using Eq 3

$$\text{Water recovery} = \frac{\text{Volume of dissociated water}}{\text{Initial volume of feed}} * 100 \quad (3)$$

## Results and Discussion

In this experimental work, the kinetic behavior of carbon dioxide in the existence of highly saline synthetic produced water of concentration 2.8wt% was studied to understand how much quantity of treated water can be obtained. The experimentations were performed at 3.0 MPa and 275.15 K to estimate the gas uptake and water recovery.

### *Carbon dioxide hydrate formation in deionized water (DIW)*

Experiments were executed with deionized water using CO<sub>2</sub> gas as the hydrate former. Figure 1 represents the temperature and uptake of CO<sub>2</sub> gas in a pure water system carried out at 275.15 K and 3.0MPa. These experimental conditions are chosen as it provides a higher driving force. The gas hydrate process is a stochastic nucleation process and is comparable to the crystallization mechanism. In a stirred reactor system, the gas dissolves in the water, which is further supersaturated forming clusters of gas-water. The amount of time it takes for these gas-water clusters to grow into stable nuclei that can continue to further expand is known as induction time. These nuclei continue to enlarge and aggregate during the growth phase. As a result, we can say that there is water present as a continuous phase constituting hydrate crystals.

Figure 1 below illustrates a typical gas uptake graph during the hydrate formation from liquid water and CO<sub>2</sub>. Three regions can be observed from figure 1(a) gas dissolution, (b) rapid hydrate development kinetics after nucleation, and (c) a phase of slow hydrate growth. The induction period is the amount of time it takes for visible nuclei to form once the gas begins to dissolve in water. Figure 1 illustrates the first nucleation occurrence within the first 54.58 mins since the beginning of the formation of the hydrate. At the point of nucleation, gas is rapidly taken up by the hydrates. From the temperature and gas uptake versus time plot when there is an abrupt spike in the temperature and correspondingly in the gas uptake profile there is a sudden spike observed this is assumed to be the starting point of the growth phase. Further, there is an initial, quick gas intake that suggests a faster rate of growth of hydrate. It is followed by a decline in the gas uptake, and finally, a steady state is reached, maybe as a result of constraints on the mass or heat transfer or simply because hydrate equilibrium is reached. In this study, depending on the type of gaseous system, the overall kinetics experiment duration ranges from 4-8 hours. As nucleation is a probabilistic phenomenon hence, the uncertainties in induction time are reduced by repeating each of the experiments four times at the same conditions, and average readings are used to evaluate their kinetic performance. Upon nucleation the gas uptake increases significantly, demonstrating the hydrate formation within the reactor. The gas uptake profile plateaued at around 4hrs. The time for these three regions from a-c varies depending on the experimental setup.

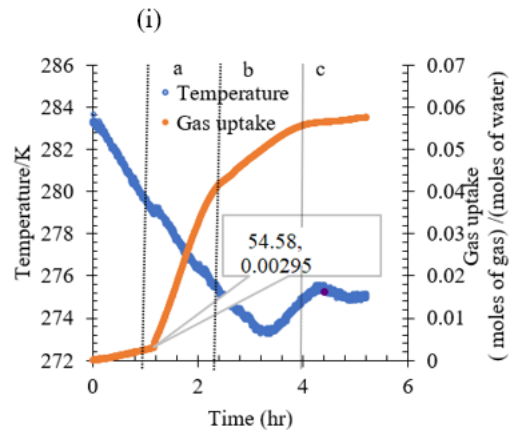


Figure 1: Temperature and gas uptake profile in pure water system

### *Carbon dioxide hydrate formation in the existence of highly saline water*

In the hydrate-based desalination reactor, the hydrates can be produced under specific temperature and pressure parameters. It is figured that throughout the formation of hydrate inside the reactor the salinity of the residual water increases gradually as the free water is converted into hydrate. It is due to the fact that the salt ions are rejected from the surface of the hydrate. In this work, kinetic experiments were executed for 180 minutes after the initial nucleation seed. Experiments were performed with produced water with a salinity of 2.8 wt% at 3.0 MPa, 275.15 K, and a stirrer speed of 450 rpm. The time taken for the first nucleation is figured to be 86 min. for the start of hydrate formation as represented in figure 2. This displays that the existence of salts inhibits hydrate formation [22-23]. The rise in temperature peak during this period is as hydrate formation is exothermic and pressure change is determined by the degree of formation of hydrate. The effect of gas uptake and liberation of heat under the influence of pressure are opposing. The gas uptake dictates the quantity of hydrate formation. The CO<sub>2</sub> gas uptake improved from 1.0 % to 5.05 % with the hydrate formation. Before the nucleation stage, the solubility of CO<sub>2</sub> increased and hence the gas uptake increased with a decrease in solution temperature. Unusually the initial rate of gas uptake of the highly saline water system in the first 60 mins is slightly higher than that of the deionized water pure system which validates well with previous works on the promotion effect in presence of salts[24-26].

It is observed that at 100 min the gas uptake in PW system decreased by 33.6% which is highly saline compared to the deionized water system having a purity of 18MΩ-cm. At 2 hrs the gas uptake decreased by 18.6% in the saline system using CO<sub>2</sub> as hydrate former. At the end of 4hrs, it is further found to decrease by 11.8%. Linga's lab reported the uptake of CO<sub>2</sub> gas as 0.0389 mol/mol when operated at 3.1 MPa and 274.2 K [27] in a stirred tank reactor using a fixed bed. Lirio's lab reported a CO<sub>2</sub> uptake of 0.038 mol/mol at 3.0 MPa and 274.15 K [28]. Higher pressures of above 3.5 MPa were not carried out in this study to consider the industrial application of hydrate-based desalination. Hence for their application, it requires reducing energy consumption thus higher pressures were not considered, and also at higher pressures CO<sub>2</sub> gets liquified.

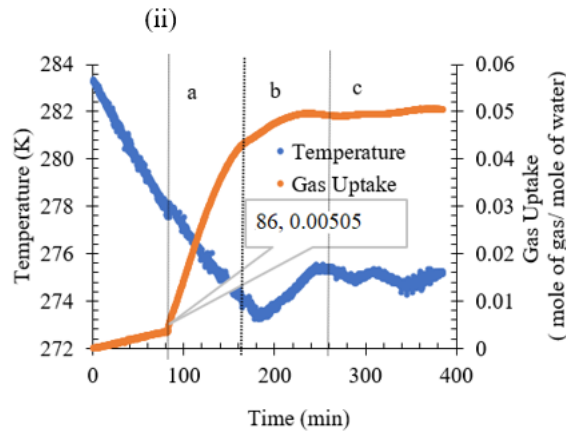


Figure 2: Temperature and gas uptake profile of PW+ carbon dioxide

Effect of salinity on the CO<sub>2</sub> hydrate formation

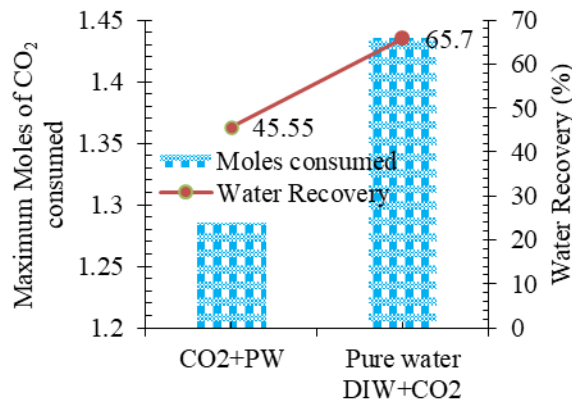


Figure 3: Comparison between moles consumed and water recovery based on the concentration

The above figure 3. shows the comparison between deionized water (DIW) 18MΩ-cm (pure water) and produced water (PW) having a salinity of 2.8wt% in terms of the amount of moles consumed and water recovery. The moles consumed and water recovery by produced water decreased by 10.43% and 30.66% compared to the pure water system. Hence, with the upsurge in salt concentration, the quantity of gas consumed declines. Since the formation of CO<sub>2</sub> hydrate initiates at the interface between water and gas, after some time of forming hydrate at the interface, the mass transfer from gas to liquid declines, and consumption of gas is reduced. As salts are dissolved in water the solubility of carbon dioxide gas in water is reduced and the strong electrostatic forces of interaction between ions and water molecules is established. These ions are solvated by the water molecules. As a result, the formation of hydrate crystals in highly saline water is more difficult compared to pure water.

**Conclusion**

Experiments were executed to study the application of the gas hydrate process for hydrate desalination of produced water, in particular, hydrate formation kinetics with respect to gas uptake and water recovery were calculated and compared with the pure deionized water. We propose to use CO<sub>2</sub> as its polar and hydrophilic to evaluate the water recovery of the process as the treated water produced is not harmful because of the presence of CO<sub>2</sub>. Results revealed that water recovery of 45.5.% is produced by treating produced water and 67.5 % water recovery in presence of

deionized water by using CO<sub>2</sub> as hydrate former at 3.0 MPa and 275.15 K. In addition, some green and biodegradable additives, can be tested to boost the kinetics of hydrate growth at the similar conditions.

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