Effect of gas type and salinity on performance of produced water desalination using gas hydrates

Hajar Fakharian, Hamid Ganji, Abbas Naderifar, Hossein Rahimi Mofrad and Majid Kakavand

ABSTRACT

In recent years, formation of gas hydrate has been considered as a suitable method for brine water desalination. In this study, for saline produced water treatment, design of experiment with two factors, the type of gas and electrical conductivity of initial brine solution (EC0) as a measure of salinity, were applied and removal efficiencies were analyzed. For this purpose, two different hydrate formers, CO2 and natural gas (NG) were separately mixed with different produced water samples. The hydrate formation reactions were carried out at 274.2 K in 35 and 95 bar, respectively, and removal efficiencies of produced water samples were tested. It has been found that with a three-stage hydrate process, 86% of dissolved minerals can be removed by the desalination process using CO2 hydrate formation gas while this amount will be 82% when NG is applied as hydrate former. Analysis of experiments indicated that the desalting efficiency depends on the hydrate-forming gas (CO2 > NG) as well as the amount of EC0 (high EC0 > low EC0).

Key words | desalination, design of experiment, gas hydrates, gas type, produced water, salinity

NOMENCLATURE

Abbreviations

C_A Ion concentration (mg/L)
DOE Design of experiment
EC Electrical conductivity (mS/cm)
HBD Hydrate-based desalination
NG Natural gas
PW Produced water
RO Reverse osmosis
TDS Total dissolved solids (mg/L)

Greek letter

η Desalination efficiency (%)

Subscript

0 Initial state (time = 0)
G Gas

INTRODUCTION

Desalination is a process that removes dissolved minerals from saline wastewater for sustainable water management in some areas of the world (Mitchell et al. 2002; Radcliffe 2006). Produced or flow back water is saline wastewater brought to the surface during gas and oil production or CO2 sequestration operation in gas and oil fields (Viel et al. 2004). Produced water (PW) associated with oil production...
generally contains liquid and gaseous hydrocarbons. Also PW contains a large range of organic compounds and dissolved salts, such as mineral ions, dispersed oil, grease, organicics, heavy metals, and other different contaminants (Abousnina et al. 2015). In areas with hard water, management of PW is highly important as it can play a fundamental role for environmental issues via safe and useful reuse or suitable discharge. The most commercially significant technologies for desalination are based on distillation, membrane, and reverse osmosis (RO) processes (Khawaji et al. 2008). Distillation is a popular method, but it is quite expensive because it requires a large amount of phase transition energy, that is the heat of vaporization of water. The application of RO in reuse of municipal wastewater effluent has dramatically increased over the past decade and is the most competing process against thermal distillation which uses semi-permeable membranes and pressure to separate salts from water (Zhu et al. 2015). Freezing is another attractive method, but is still not widely used commercially (Han et al. 2017).

Hydrate as a technology for desalination was developed way back in the 1940s and has gained increased attention from the 1970s until recent years (Parker 1942; Park et al. 2011). Hydrate formation can remove salts and other impurities of brine water due to the chemical structure of hydrate. When hydrate is formed, clean water is obtained after dissociating the hydrate particles (Cha & Seol 2013; Han et al. 2014). Gas hydrate technology is still under development, but when applicable at larger scale, it could be an inexpensive alternative to the traditional thermal and membrane desalination processes (Ghalavand et al. 2015). Also, because of the additional hydrate formers (guest), gas hydrate forms at higher temperature than the freezing point of ice which can improve energy efficiency (Han et al. 2017).

Natural gas hydrate is composed of water and a certain number of natural gas molecules under favorable conditions of pressure and temperature (Rahimi Mofrad et al. 2016). The main structures of hydrates are classified as sI, sII, and sH (Sloan & Koh 2007; Fakharian et al. 2012). Some researchers have reported that hydrate-based desalination (HBD) process can compete with other conventional technologies such as distillation, membrane, and RO processes (Barduhn et al. 1962; Williams 1964; Barduhn 1967; Kubota et al. 1984; Makogon 1997; Javanmardi & Moshfeghian 2003; Boysen 2010; Fakharian et al. 2012; Sangwai et al. 2013; Kang et al. 2014; Karamoddin & Varaminian 2014; Lee et al. 2016). In previous works, light hydrocarbons or chlorofluorocarbon refrigerants were applied as hydrate formers for desalination of seawater, since they are appropriate formers that work with low pressure relative to other hydrate formers (Barduhn et al. 1962; Kubota et al. 1984; Karamoddin & Varaminian 2014). Although they require lower pressure for operation, environmental problems have limited their use. Also, most of the research in the field of HBD is on seawater, while wastewater produced in oil and gas fields has salinities greater than seawater (Lee & Neff 2014). Cha & Seol (2015) used HBD to recover usable water from PW. They introduced cyclopentane (C\textsubscript{5}H\textsubscript{10}) and cyclohexane (C\textsubscript{6}H\textsubscript{12}) as secondary hydrate guests so that the operation temperature could be increased. Although C\textsubscript{5}H\textsubscript{10}/C\textsubscript{6}H\textsubscript{12} is nearly immiscible with water, tiny drops may remain in the clean water. In addition, their study was limited to a single PW sample.

It seems that a carefully developed HBD process is required to investigate various factors that affect the removal efficiency. Karamoddin & Varaminian (2014) used R141b as a hydrate former and investigated the effect of initial temperature and concentration of NaCl on removal efficiency. Han et al. (2014) investigated the HBD process using C\textsubscript{3}H\textsubscript{10} as a hydrate former and effective post-processing operations to improve the competitiveness of the hydrate method for desalination of synthetic seawater. In that research, optimal operation temperature and concentration of C\textsubscript{3}H\textsubscript{10} were obtained from the measured results. Recently, they have applied successive washing treatment with 274.15 and 277.15 K temperature freshwater. In this work different amounts of washing water have been applied and major cations and anions in seawater have been analyzed in each treatment step (Han et al. 2017).

Since most of the researchers use CO\textsubscript{2}, light hydrocarbons, or chlorofluorocarbon refrigerants as hydrate former in HBD for seawater, further study on desalination of PW with these and other hydrates forming gases may be useful. In this work, to determine the relationship between factors affecting HBD process and their removal efficiencies, a design of experiment (DOE) incorporating two factors, type of gas and electrical conductivity of initial brine solution (EC\textsubscript{0}), has been done to analyze the removal efficiencies. For this purpose, two hydrate formers, CO\textsubscript{2} and natural gas (NG), were separately mixed with different produced water samples and hydrate formation reactions were carried out.
The reason for using NG instead of methane was its cheaper price and easier accessibility. In addition, NG hydrate is formed at milder conditions than that required for methane.

In this research, the desalination efficiency of the third stage with NG/CO₂ hydrate formation was investigated and, finally, the usable range of initial total dissolved solids (TDS) was discussed in a NG/CO₂–HBD system.

EXPERIMENTAL

Materials

High purity CO₂ (99.99%) and natural gas (NG) with composition as specified in Table 1 were used to form hydrate with produced water. The molar composition of the natural gas components was obtained using gas chromatography.

For synthesized PW, sodium chloride (NaCl; Kimia, >99.5%), potassium chloride (KCl; Merck, >99.5%), calcium carbonate (CaCO₃; Merck, >99.5%), calcium chloride (CaCl₂; Merck, 98%), magnesium chloride hexahydrate (MgCl₂·6H₂O; Arastoo Chemical Industry, >99.5%), sodium sulfate anhydrous (Na₂SO₄; Merck, 99%), hydrogen chloride (HCl 1N solution, Merck), and xylene (C₈H₁₀; Merck, 99.8%) were used.

PW samples

To prepare PW synthetic samples, three different PW samples were collected. The first real PW sample was obtained from Asmari reservoir in Shadegan oil field of Khuzestan Province, Iran (31.3273° N 48.6940° E). The second real sample was taken from Bangestan reservoir in the same oil field and the third one was obtained from oil and gas fields throughout 34 states provided by the U.S. Geological Survey (Cha & Seol 2013). Table 2 shows the specifications of the three mentioned prepared samples.

Apparatus

The experimental setup used for this research work has been addressed in Fakharian et al. (2017). It contains a hydrate reactor with a volume of approximately 300 cm³, a cooling medium circulatory system to control the temperature, a gas cylinder to inject the gas, and a mixer to mix the contents of the hydrate reactor. A 0.5 psi scale pressure transducer (accuracy approximately 0.5%) and a 0.1 K scale thermocouple (accuracy approximately 0.4%) were used to measure the pressures and temperatures. A data collection system was incorporated to record the data during the process and, finally, a separating container was used to drain the condensed concentrated salty water.

Procedure

Factorial design experiments

DOE is a systematic method to determine the relationship between factors affecting a process and the output of that process. The principles of statistically designed experiments

<table>
<thead>
<tr>
<th>Component</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>n-C₄</th>
<th>i-C₄</th>
<th>n-C₅</th>
<th>i-C₅</th>
<th>C₆</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar composition (%)</td>
<td>87.5</td>
<td>4.8</td>
<td>1.16</td>
<td>0.44</td>
<td>0.32</td>
<td>0.05</td>
<td>0.07</td>
<td>0.01</td>
<td>4.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>K⁺</th>
<th>SO₄²⁻</th>
<th>Mg²⁺</th>
<th>HCO₃⁻</th>
<th>Na⁺</th>
<th>Cl⁻</th>
<th>Ca²⁺</th>
<th>EC (mS/cm)</th>
<th>pH</th>
<th>TDS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>985</td>
<td>694</td>
<td>1,512</td>
<td>90</td>
<td>15,200</td>
<td>120,500</td>
<td>11,720</td>
<td>210</td>
<td>5.3</td>
<td>171,000</td>
</tr>
<tr>
<td>2</td>
<td>490</td>
<td>291</td>
<td>607</td>
<td>512</td>
<td>27,500</td>
<td>48,744</td>
<td>3,900</td>
<td>130</td>
<td>5.6</td>
<td>86,460</td>
</tr>
<tr>
<td>3</td>
<td>6,114</td>
<td>1,132</td>
<td>1,028</td>
<td>656</td>
<td>24,609</td>
<td>53,621</td>
<td>4,875</td>
<td>124</td>
<td>7.14</td>
<td>89,254</td>
</tr>
</tbody>
</table>
are determination of the response which reflects the aim of the study, factors and their levels and choice of the experimental design, and statistical analysis of the data (Seki et al. 2006; Fakharian et al. 2014). DOE encompasses many types of experimental designs and different designs are ideal for different objectives. Factorial designs are ideal for factor screening experiments and systems in which interaction between factors is thought to be significant (Narang et al. 2012). In this study, factorial design with two factors, the type of gas and electrical conductivity of the initial brine solution (EC0), was applied to evaluate their impact on the removal efficiency as a response. The type of gas was investigated on two levels (NG and CO2) and six levels were selected for electrical conductivity of initial brine solution (EC0) according to the compositions of the three samples shown in Table 2. Six PW samples were synthesized by chemicals mentioned in the section ‘Materials’. The number of experiments conducted was considered as $2^1 \times 6^1$ runs. Table 3 summarizes the mentioned two factors and their respective levels. Data analysis was performed using Minitab release 14 software.

**Experimental section**

The experimental conditions are summarized in Table 4. The reactor is first pressurized to 110 bars with inert gas (N2) and left for 24 h at 293.2 K to ensure that the pressure remains constant with no leakage. Then, it is depressurized, washed with distilled water and loaded with 100 cm$^3$ of synthesized PW. The reactor is purged with CO2/NG to ensure the absence of any other gases. Afterwards, the system is cooled down to the suitable conditions for hydrate formation. After reaching equilibrium, the reactor is pressurized with CO2 or NG. Then, the mixer is turned on with the rates given in Table 4.

To reach CO2 hydrate formation, after reducing the pressure, the gas cylinder valve is opened up to a constant pressure (P1 = 35 bar) to achieve hydrate slurry. During CO2/NG hydrate formation (first, second, and third stages), temperatures and pressures are recorded every 20 seconds to monitor hydrate formation. Gas volume is assumed to be constant. To ensure the data accuracy and repeatability, the experiments of each sample have been repeated twice using two reactors at the same conditions. Since the main objective of this research was to investigate the water salt removal efficiency not hydrate nucleation and growth rate, the experiments have only been repeated twice. The reported results are the average of two repeated experiments. In fact, hydrate formation in each reactor is initiated at the same initial pressure and stopped at the same final pressure for each stage. Although the time to reach the same final pressure is a bit different in two reactors, the salt removal efficiencies are approximately similar.

After hydrate formation, the residual salty water is removed from the reactor and the formed hydrate is rinsed with fresh water to improve salt removal efficiency and, finally, hydrate is dissociated to produce fresh water.
the hydrate is dissociated, the EC of the formed water is measured using a conductivity meter (WTW Multiline P4) with an accuracy of 0.1 μS/cm. Equation (1) is used to calculate the removal efficiencies for the first, second, and third stages in the primary PW and the desalinated water.

\[ \eta = \frac{EC_0 - EC}{EC_0} \times 100 \]  

(1)

where \( \eta \) is the desalination efficiency and \( EC_0 \) and \( EC \) are the electrical conductivity of initial and final brine solutions (Karamoddin & Varaminian 2014).

RESULTS AND DISCUSSION

Analysis of experimental design

The design matrix of factors with values and the responses (%efficiency) measured in each factorial experiment are shown in Table 5. The order in which the experiments were made was randomized to avoid systematic errors (Std order column).

Analysis of DOE indicated that the desalting efficiency (\( \eta \)) for the first stage depends on the hydrate-forming gas and the amount of \( EC_0 \). The hydrates formed with CO2 had higher average desalting efficiency compared to that of NG (\( \eta_{CO2} > \eta_{NG} \)). Figure 1 shows a picture of NG/CO2 hydrate crystals formed in the PW (sample 2) at the end of the first stage which confirms the results. The hydrate formed with CO2 is well packed in contrast to NG hydrate which is spongy. More packed CO2 hydrate may correspond to the lower quantity of salt entrapped between the crystals and, therefore, the water produced by hydrate dissociation will be more desalinated.

In order to analyze DOE and significance of the main factors and their interactions on the response, analysis of variance (ANOVA) was used. Table 6 shows the sum of squares (SS), mean squares (MS), F-values and P-values. Since the P-values are less than 0.05, the main effects are significant factors in the level of \( \alpha = 0.05 \) and the interaction between type of gas and EC is negligible. Comparison of the P-values shows that EC has a greater effect on desalting efficiency than gas type. Also, the R-squared statistic indicates suitable accuracy of the results.

Figure 2 shows the main effects plot for %efficiency. The average desalting efficiency increases with increasing the salinity of the initial brine solution. When the water initial electrical conductivity increases, the inhibition effect increases accordingly and then the quantity of hydrate decreases (Fakharian et al. 2017). The lower quantity of hydrate corresponds to lower quantity of salt

Table 5 | Factors, levels, and the results of the factorial design

<table>
<thead>
<tr>
<th>Std order</th>
<th>Run order</th>
<th>EC</th>
<th>gas</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>151</td>
<td>NG</td>
<td>47.35099</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>132</td>
<td>NG</td>
<td>44.31818</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>132</td>
<td>CO2</td>
<td>47.72727</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>151</td>
<td>CO2</td>
<td>51.3245</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>130</td>
<td>CO2</td>
<td>47.69231</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>173</td>
<td>NG</td>
<td>56.6474</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>114</td>
<td>NG</td>
<td>32.89474</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>124</td>
<td>CO2</td>
<td>36.29032</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>114</td>
<td>CO2</td>
<td>45.08772</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>124</td>
<td>NG</td>
<td>34.59677</td>
</tr>
<tr>
<td>12</td>
<td>11</td>
<td>173</td>
<td>CO2</td>
<td>59.53757</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>130</td>
<td>NG</td>
<td>42.61538</td>
</tr>
</tbody>
</table>

Table 6 | Analysis of variance

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of Freedom</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>5</td>
<td>634.38</td>
<td>634.38</td>
<td>126.88</td>
<td>17.97</td>
<td>0.003</td>
</tr>
<tr>
<td>Gas</td>
<td>1</td>
<td>71.23</td>
<td>71.23</td>
<td>71.23</td>
<td>10.09</td>
<td>0.025</td>
</tr>
<tr>
<td>Error</td>
<td>5</td>
<td>35.31</td>
<td>35.31</td>
<td>7.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>740.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( S = 2.65737; R-Sq = 95.23\%; R-Sq(adj) = 89.52\% \).
entrapped between the hydrate crystals and the water produced by hydrate dissociation will be more desalinated. Only in EC = 114 mS/cm was an increase in efficiency perceived that may be attributed to the presence of xylene as representative organic components in in situ PW. Also, the average desalting efficiency of CO₂ hydrate is higher than that of NG (η CO₂ = %49 > η NG = %43) which can be related to the structure of CO₂ hydrate, which is more packed in comparison with that of NG, as already discussed.

As described in the analysis of the ANOVA table, the interaction between the kind of gas and EC is negligible. The interaction plot for %efficiency (Figure 3) confirms this result. In fact, when the lines are parallel in the

Figure 2 | Effect of main parameters on salt removal efficiency.

Figure 3 | Interaction effects plot.
interaction plot, it appears that the interaction of the main factors on the response variable is not significant (Montgomery 2008). Only in EC = 114 mS/cm does the corresponding line have a steeper slope, which means that the more intense interaction between the main factors is because of the presence of organic components.

**Desalination efficiency of the third stage with NG/CO₂ hydrate formation**

In order to achieve appropriate salt removal efficiency, additional repetitive stages of hydrate formation process are necessary to trap salty water between hydrate crystals. Consequently, the second and third stages were carried out with the desalinated water of the first stage. As Table 4 shows, the second and third stages of desalination are faster than the first stage for both NG and CO₂ hydrate formation. Increase in the rate of hydrate formation in the second and third stages may be due to the hydrate memory and reduction of TDS amount in the desalinated water of each stage. Table 7 shows the salt removal efficiency of three stages for sample 2. As depicted in Table 7, desalination efficiency increases with increase of the stage and reaches approximately 82% and 86% after three stages of NG/CO₂ hydrate formation, which in turn decreases the EC of the used PW to 23.7 and 18.3 mS/cm, respectively. The water with this EC level can be used for farm domestic and livestock uses for both NG and CO₂ hydrates. The higher efficiency of the third stage is because of the lower EC of the formed water in the former stage. Thus, to improve the water quality, the number of stages should be increased.

To find an applicable limit of TDS of PW using HBD, some experiments were performed on sample 1 with a high salinity of 80, 70, 60, and 50% TDS (samples 1–0 to 1–4 in Table 8). For PW desalination, NG/CO₂ hydrate was not formed in sample 1, after approximately 20 and 5.5 hours, respectively. The inhibition effect is due to ionization of salts in aqueous phase. Indeed, the preferential ion dipole interactions are more intense than interactions between H₂O molecules such as hydrogen bonding and/or Van der Waals forces (Nazari et al. 2013).

As Table 8 shows, NG/CO₂ hydrates were not formed in the PW samples with EC greater than 173 mS/cm (which is equivalent to TDS of 160,000 mg/L) at operating conditions. In other words, the limit for PW desalination with NG/CO₂ hydrate formation method is EC = 173 mS/cm, which is equivalent to TDS = 160,000 mg/L. Additionally, desalination efficiency increases with increasing the percentage of dissolved salts. When the water salinity increases, the inhibition effect also increases and, consequently, the amount of hydrate decreases. The lower amount of hydrate corresponds to the lower amount of salt entrapped between

<table>
<thead>
<tr>
<th>Stage</th>
<th>EC (mS/cm)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NG</td>
<td>CO₂</td>
</tr>
<tr>
<td>1</td>
<td>74.6</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>34.3</td>
<td>34.7</td>
</tr>
<tr>
<td>3</td>
<td>23.7</td>
<td>18.3</td>
</tr>
</tbody>
</table>

**Table 8** | Hydrate formation in samples with different salinity

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Percentages of sample 1 dissolved ions (%)</th>
<th>EC₀ (mS/cm)</th>
<th>The first stage EC (mS/cm)</th>
<th>Efficiency for the first stage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NG</td>
<td>CO₂</td>
<td>NG</td>
</tr>
<tr>
<td>1–0</td>
<td>100 (sample 1)</td>
<td>210</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1–1</td>
<td>80</td>
<td>193</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1–2</td>
<td>70</td>
<td>173</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>1–3</td>
<td>60</td>
<td>151</td>
<td>79.5</td>
<td>73.5</td>
</tr>
<tr>
<td>1–4</td>
<td>50</td>
<td>132</td>
<td>73.5</td>
<td>69</td>
</tr>
</tbody>
</table>
the hydrate crystals and so the water recovered by hydrate dissociation will be more desalinated.

CONCLUSION

This study investigates the effect of gas type and salinity on performance of produced water desalination using gas hydrates. Analysis of the DOE indicated that the desalting efficiency depends on the hydrate-forming gas (CO\textsubscript{2} > NG) and the amount of EC\textsubscript{0} (high EC\textsubscript{0} > low EC\textsubscript{0}). Moreover, electrical conductivity of water formed by hydrate dissociation was examined in three stages to investigate the removal efficiency. The results showed that the salinity of produced water can be decreased by approximately 86% and 82% using hydrate formation with CO\textsubscript{2} and NG as guest gases, respectively. In addition, this study illustrated that the CO\textsubscript{2}/NG hydrate formation can be used for desalination of produced waters with up to 160,000 mg/L TDS at the operating conditions of experiments.

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