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Desalination of high salinity produced water using natural gas hydrate

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ABSTRACT

Hydrate-based desalination was suggested as a new method in recent years. In this study, compressed natural gas (CNG), mixed with various produced water samples and the hydrate formation reactions were performed at the pressure of about 95 bar and temperature of 274.2 K. After hydrate formation, the concentrated salty water was extracted from the reactor and the formed hydrate was washed with a suitable amount of fresh water to successfully improve desalination efficiency. Then, the hydrate was dissociated to produce fresh water. Desalination efficiencies for dissolved mineral extraction from produced water samples were measured and it has been found that with 3-stages hydrate process, 79.5%--84.3% of dissolved mineral components will be removed using gas hydrate formation. This study indicated that the CNG hydrate formation for desalination can be applied for produced waters with initial total dissolved solids (TDS) less than 160,000 mg/L.

Abbreviations

AAS	atomic absorption spectroscopy
CH	cyclohexane
CP	cyclopentane
EC	electrical conductivity (mS/cm)
HBD	hydrate-based Desalination
PW	produced water
RO	reverse Osmosis
TDS	total dissolved solids (mg/L)

1. Introduction

Gas hydrates are crystalline complexes composed of water and gas molecules. The guest molecules are decoyed in host molecules cavities that are composed of hydrogen bonding in water. Typical natural gas molecules include CH_4, C_2H_6, C_3H_8, and CO_2 [1]. Gas hydrates can form in three typical crystal structures, that are sI, sII and sH [1–2].

Natural gas hydrate formation and dissociation processes have many applications in energy and environmental aspects; such as fuel storage/transportation, recovery of energy, safely and desalination of seawater [3]. Hydrate-based desalination (HBD) process was offered in the 1940 s and obtained notable attention in the 1960 s until recent years considering the capability of gas hydrates [4–6]. On the other hand, hydrate formation can remove salts and other impurities of brine water because of the chemical structure of hydrate. After hydrate formation, the hydrate is dissociated and desalinated water is obtained [7].

The main investigations on HBD are being focused on the use of crystalline complexes for the seawater desalination but as yet no pilot plant for it exists, however it continues to compete with conventional techniques [8–9]. HBD has been discussed as an appropriate method that can be used instead of usual methods such as distillation, membrane processes and reverse osmosis (RO) [7,5, 10–15]. Two of the most commercially significant technologies are based on distillation and RO processes [16]. 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 [7]. RO is the most competing process against thermal distillation which uses semi-permeable membranes and pressure to separate salts from water. Pre-treatment of RO method is an important step, due to the nature of membrane design, that is, only one-way flow through membrane [17,18]. Makogon reported that HBD process can be cheaper than other methods such as thermal and membrane processes [19]. Recently, some researchers studied various refrigerant/Freon hydrates. Kubota et al. [20] and Barduhn et al. [10] applied this analysis for different refrigerant hydrates such as R152a and R21 hydrates formation. Also the results of equilibrium temperature were presented for hydrate formation in brine solution by Sandia National Laboratories [21]. In fact, refrigerant/Freon as hydrate former is appropriate for engineering applications; particularly for desalination operations because they are atmospheric hydrate formers that cause to avoid working with high pressure

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Nomenclature

C_A	ion concentration (mg/L)
n	the number of moles (mol)
P	pressure (MPa)
ΔP	pressure drop (MPa)
R	universal gas constant (8.314 j/mol/K)
T	temperature (°K)
t	time (h)
V	volume (cm^3)
Z	gas compressibility factor
Greek letter	
η	desalination efficiency (%)
Subscript	
0	initial state
G	gas

process [5], but environmental problems have restricted their application. Park et al. applied an equipment for seawater desalination that continuously produced and pelletized CO_2 hydrates by a squeezing operation of a dual cylinder unit [14]. Also, before and after the hydrate process, dissolved ions were analyzed [22]. Recently the effects of salinity on the equilibrium of CO_2 and R134-a gas hydrates has been investigated by tracing the changes of operating temperature and pressure [23]. Salt removal using cyclopentane hydrate formation and washing treatment for seawater desalination was investigated by experimental measurement of the salt concentration in filtered water and water retrieved from hydrate crystals [17].

One of the saltiest water is Produced Water (PW) that can be reused after treatment. On the other hand, oil and gas operations produce a large volume of waste water that is considered as the largest byproduct of oil and gas generation [24]. About ninety percent of the PW during hydrocarbon production is injected into the well and ocean, but because of transportation and disposal costs, deep injection is very expensive [24–25]. PW contains different impurities that should be removed before any useful applications. The main contaminants of produced water include high level of TDS, oil and grease, salts, organics, suspended solids and different other contaminants. These contaminants may possibly include heavy metal and radio nuclides [25–27]. PW chemical composition varies over a large range and depends mainly on attributes of reservoirś geology. The composition of PW may also change slightly through the production lifetime of the reservoir [28]. In areas with hard water, useful reuse of PW such as industrial applications and groundwater recharge has become a significant option for PW management. So, treatment of PW using adsorption, oxidation, stripping and RO have been widely investigated and it is technically feasible and economically reasonable [7,29].

As mentioned before, many researchers in the field of HBD have investigated on seawater; while various produced waters are saltier than seawater [30]. Only a few studies focused on PW desalination using hydrate formation. Cha et al. [7], have proposed using secondary hydrate guests such as cyclopentane (CP) and cyclohexane (CH) to reduce temperature for the PW HBD process. Because CH/CP is immiscible in water, after hydrate formation, water will combine with CH/CP to form SII hydrates. The hydrate dissociation process should be exactly controlled, because the tiny drops of CH/CP may remain in the desalinated water [31,22]. Therefore, the use of additives such as CH/CP is restricted. In addition, their researches were also restricted to a single PW sample. Also, further desalination research with a different hydrate forming gas should be carried out, since most of the research uses carbon dioxide (CO_2) or refrigerant/Freon as hydrate former in the field of HBD.

In the present study, CNG hydrate former is introduced in a HBD system for high salinity PW. Electrical conductivity (EC) of water produced from hydrate dissociation has been measured to check the removal efficiency of salt. Desalination efficiency of dissolved mineral components has been also examined for PW samples. In addition, for the first time, various synthesized PW with different salinity were tested to discuss the usable range of initial total dissolved solids (TDS) in a CNG- HBD system.

2. Experimental

2.1. Materials

Compressed natural gas (CNG) with composition specified in Table 1 was used to form hydrate with produced water.

For synthesized produced water, Sodium chloride (Kimia, > 99.5%), Potassium chloride (Merck, > 99.5%), calcium carbonate (Merck, > 99.5%), calcium chloride (Merck, 98%), Magnesium chloride hexahydrate (Arastoo chemical industry, > 99.5%), Sodium sulfate anhydrous (Merck, 99%), and Hydrogen chloride 1 N solution (Merck) were applied.

2.2. Samples of PW

To make real PW synthetic samples, two various PW samples were collected from oil fields and their composition were analyzed. The first PW sample was obtained from Bangestan reservoir in the Shadegan oil field of Khuzestan Province in Iran. Organic components from *in situ* PW were not contained into the formulation of synthesized PW since the evaluation of these compounds was not feasible (Table 2).

The second sample was based on information of Asmari reservoir in the same oil field which Table 3 shows its specification.

By applying the composition of above mentioned real samples, six PW samples were synthesized by chemicals listed in the materials section. The first synthetic sample was prepared applying the chemical composition of Bangestan reservoir while the second

Table 1
Molar composition of the natural gas components.

Component	C_1	C_2	C_3	n-C_4	i-C_4	n-C_5	i-C_5	C_6	N_2	CO_2
Molar composition (%)	87.5	4.8	1.16	0.44	0.32	0.05	0.07	0.01	4.4	0.8

Table 2
Analysis of mineral ions in Bangestan PW sample (sample 1).

Item	Ion concentration (C_{A0}) (mg/L)							EC (mS/cm)	pH	TDS (mg/L)
	K^+	SO_4^{2-}	Mg^{2+}	HCO_3^-	Na^+	Cl^-	Ca^{2+}			
Value	490	291	607	512	27,500	48,744	3900	130	5.6	86,460

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