

# Advancement in Gas Hydrate Water Based Produced Water Desalination: An Overview

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## ABSTRACT

In the petroleum industry, produced water is regarded as the significant waste stream that constitutes a comparatively higher fraction of hydrocarbons, heavy metal ions & various contaminants. Because of the minimal quantity of freshwater, there is a need to investigate other resources. Using produced water, which is available in plenty, seems to be a good resource to obtain freshwater using gas hydrate water-based desalination. Few of the current researchers have focused the attention on desalination with hydrates which can produce pure water more cheaply compared to conventional technologies. This paper provides a brief review of the current researcher's accomplishments in the desalination of highly saline water or produced water through gas hydrate technology. It is apparent from the literature that suitable hydrate formers appreciably improve the thermodynamic conditions of hydrate formation. This review will deliver the outline for the prospective implementation of gas hydrate-based water desalination in treating produced water. In a word, treating produced water by hydrate-based technology hopefully seems to be environment friendly, low-cost, and widely used desalination technology in the future.

**Keywords:** Desalination, freshwater, gas hydrate, produced water

## 1. INTRODUCTION

Petroleum is a foremost resource of energy and income that is intended for several countries worldwide at present, and its production has been regarded as the most significant industrial activity in the twenty-first century [1]. Oil and gas extracted from petroleum oilfields in various regions of the world are accompanied by salty water called produced water. Produced water or flow back water is defined as the highly saline water that is brought to the surface at the time of production of oil and gas [2]. During petroleum extraction, they produce a vast quantity of wastewater that is observed as the most significant derivative of oil and gas production [3]. Nearly 90% of the produced water is introduced into the well during hydrocarbon production to increase oil production; however, due to transportation and dumping costs, deep injection is very expensive [3-4]. With an increase in population, land usage, changes in weather across the globe, the demand for freshwater has increased widely. As huge quantities of produced water are produced, several countries have oilfields, that are mostly water-stressed-out nations that are increasingly focusing on attempting to figure out effective and efficient treatment techniques to enhance their inadequate water resources [5]. Hence, an economical treatment technique that might convert produced water into an added benefit is considered as prior importance.

The significant water resources is produced water. When oil & natural gas is produced, water is also produced along with them from the well. The obtained produced water ranges from freshwater to over-saturated containing many chemical constituents like salts, minerals, dissolved organic and inorganic components, radionuclides, and naturally occurring radioactive materials [4,6-7]. Produced water is figured to have higher salt content compared to seawater. It is considered as the significant stream of wastewater generated from the oil & gas industries, approximate greater than 70 billion barrels per annum in the year 2009 throughout the world, out of which 21 billion barrels are generated by the United States only [8]. Produced water results during extraction, which produces a mixture of water & oil, and this water can be further injected into the oil well to fetch the deep oil to the surface level, which is termed as produced water. The chemical composition changes and relies mostly on the reservoir's geographical location. The constitution of produced water varies fairly throughout the production lifetime and as well as the age of the well. As the well ages out more quantity of produced water obtained compared to oil produced or in other words the ratio of water to oil obtained is figured to be 3:1. The conductivity of produced water varies from 4200 to 180,000  $\mu\text{S}/\text{cm}$  [9]. As produced water has various contaminants with changing concentrations; hence several treatment techniques are required for produced water treatment. Extensive techniques for produced water treatment have been communicated [5, 10-13]. At the same time, as a result, it's challenging to decide the appropriate treatment to eliminate the majority of impurities from produced water. Universally

produced water treatment procedure consists of three foremost levels being pre-treatment followed by major treatment and polishing stage. An amalgamation of physical, chemical, biological and membrane treatment methods ought to be implemented for the attainment of pure water. This article reviews regarding the treatment of produced water by gas hydrate technology and, yield reusable water that can be used by industries and agricultural sector through minimal negative influence on the environment.

## 2. CONVENTIONAL AND INNOVATIVE DESALINATION METHODS

Desalination is a method of salts removal from saline water using a cost-effective process either by application of heat or using membranes to convert them to freshwater. Currently, several countries rely on desalination, techniques predominantly the Middle East, mainly due to the region's petroleum reserves that continue to put the cost of energy low. Researchers evaluated that nearly 75 million people globally obtain fresh water through the desalination method [14]. The global worldwide percentage distribution of desalination systems as per the geological region [15] is represented in Figure 1.

Desalination techniques are classified based on three main categories, specifically: (i) thermal based systems are based on evaporation and condensation that are the major processes implemented to separate salts (ii) pressure based systems rely on applying pressure on the saline water to force freshwater alone all the way through the membrane, withdrawing behind salts (iii) chemically-activated methods. Thermal based systems comprise multistage flash distillation (MSF), multiple-effect distillation (MED), vapor compression distillation (VCD), humidification-dehumidification desalination (HDH), solar distillation (SD), and freeze-thaw methods. All these methods require heat to boil the saline water to convert to vapor, thereby separate salts. Pressure applied techniques utilize a semi-permeable membrane to segregate salt and water. It consists of technologies like reverse osmosis (RO), forward osmosis (FO), electrodialysis (ED), and nanofiltration (NF). Chemically-activated desalination comprises ion-exchange desalination (I.Ex), liquid-liquid extraction (LLE), and gas hydrate (G.Hyd) technologies [16-18].

MSF works on the principle wherein evaporation is achieved by reducing pressure through different stages to produce fresh water. Multistage distillation setups generate around 60% of desalinated water across the globe. This procedure is regarded as the foremost cost-efficient method in producing freshwater, and the cost of energy is comparatively less. Multi-effect distillation also works on the same principle as MSF apart from the fact that saline water is heated with the help of steam in the tubes in the first stage. Then, the resultant vapor is used in subsequent stages to evaporate the water. This procedure functions at a lesser temperature compared to MSF. In VCD, the gas produced in the evaporator compartment is compressed thermally or

either mechanically to increase temperature and vapor pressure. In HDH, heat transfer happens directly among air and vapor. In thermal processes, heat is exchanged to boil or else to freeze the saline water to change to vapor or ice so that salts are eliminated.

Reverse osmosis is implemented so that highly saline water can pass via a semi-permeable membrane by applying hydrostatic pressure much greater than osmotic pressure. Electrodialysis utilizes the driving force of electric potential to attract and move dissimilar ions through a semi-permeable membrane. Forward osmosis is an osmotic procedure that makes use of a semi-permeable layer to result in separating water from dissolved salts using osmotic pressure as a driving force among high concentration and lower concentration solutions.

Among the ones stated above, the most commercially and widely implemented desalination processes are the MSF and RO. MSF distillation is predominantly suitable to produce freshwater from saline water since the energy cost is comparatively lower. Though MED can contend technically and economically with MSF in some situations whereby using lower quality heat media than MSF, it has enhanced compatibility with indirect solar desalination, and is further suitable and reliable for lower capacity applications. Multi vapor compression desalination is predominantly appropriate to mixtures having very high total dissolved solids and can accomplish higher recovery compared to MSF or MED. Some estimate shows that MSF and reverse osmosis accounts for 40 % to 50 % of the world's total desalination capacity. MSF technology is observed to be an industrial scale with a capacity of over 5000 m<sup>3</sup>/day while RO is more intensely used for small scale production activities. However, the RO mechanism gained importance in desalination due to its lower cost and simplicity.

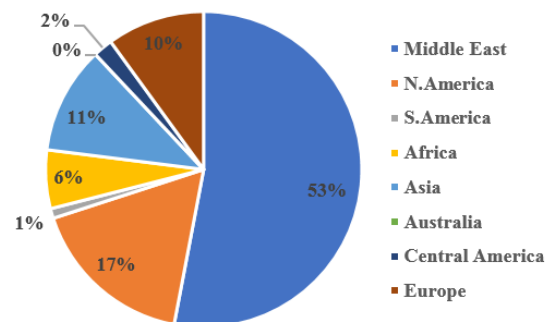


Figure1 Worldwide desalination systems per geographical area (%) [15]

As the existing thermal treatment technologies and mechanical treatment methods are not able to eliminate every minute suspended particles or harmful dissolved organic and inorganic compounds. Apart from this, the disadvantages being that Reverse Osmosis (RO) involves significant capital investment and maintenance, while Multistage Flash distillation (MSF) is furthermore an energy exhaustive process [19]. Also, these advanced techniques are way expensive to produce small volume

production, making them unsuitable for rural applications [20]. In order to address the above-listed drawbacks or disadvantages, new technologies or techniques must be explored for a practical and economically feasible solution for sustainable development.

Numerous state-of-the-art techniques have been examined with imminent for forthcoming desalination applications [21]. Electro-deionization (EDI) is an amalgamation of electrodialysis and ion exchange process. Other innovative techniques comprise membrane-based separation, or amalgamations of the membrane/ distillation, and freezing with gas hydrates. Even though these methods found to be more dependable, yet these require constant improvements in research and development to make the water purification technologies more economical and approachable [22]. Amongst these novel techniques, gas hydrates look to be the best choice to be explored as the future desalination technology [14]. The implementation of gas hydrate based desalination procedure is appealing for the reason that for gas hydrate formation the critical source is water which is easily available and hydrate former gas together form hydrate at appropriate low temperature and higher pressure so that the hydrate formed is later dissociated to pure water and gas leaving behind the residual water in the reactor [23]. Additionally, it is delineated that desalinating highly saline water through gas hydrate technology consumed less energy, accompanied by the additional benefit of avoiding pretreatment [24]. The notion of using gas hydrate-based water desalination is not the latest technique. Gas hydrate-based water desalination was suggested and put forth in the 1940s and, after that, subsequently progressed little by little [25-26]. Later, researchers developed a few suggestions regarding extracting fresh water from seawater by using gas hydrates [22]. Throughout this period, researches focused on using different hydrate formers and various designs of equipment for the process to make it viable. To date, the problems related to sorting out hydrate from residual/concentrated brine solution, and in addition to separating hydrate former and pure water; remain as the technological hindrances. There is a necessity to resolve various complex and fundamental aspects, prior to the gas hydrate-based water desalination process becomes commercial. Many investigators preferred to examine and explore the technical queries relating to nucleation, agglomeration, and hydrate growth, metal ion removal, separation of hydrate from brine, and reuse of the guest molecule.

As many researchers in the area of hydrate-based desalination have experimented on seawater with respect to the feasibility of this technology; where the same technique can be implemented in treating produced water that is very saltier compared to seawater [27]. Not many studies dealt with treating produced water using hydrate-based water treatment. This review article puts forth the developments of gas hydrate-based water desalination method in treating highly saline water that is produced water and lists the progress on hydrate formers used, formation enhancements based on up to date literature.

### 3. OVERVIEW OF GAS HYDRATES

Gas hydrates are crystalline ice-like, nonstoichiometric made of water as host molecule, and gas as hydrate former as shown in Figure 2. such as  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , etc. that are held by hydrogen bond, that form at a lower temperature usually  $< 20^\circ\text{C}$ , and higher pressure usually  $> 30$  bar [28]. It is noticed that  $1\text{m}^3$  of hydrate can generate up to  $164\text{m}^3$  of gas and  $0.8\text{m}^3$  of pure water at standard temperature and pressure conditions if dissociated. Based on the quantity of pure water generated per  $\text{m}^3$  of hydrate, the process of using gas hydrate for desalination seems promising. Owing to the existence of a large quantity of water in the hydrates, the physical parameters like density, refractive index, and specific heat seem to be analogous to the ice with some deviations. Gas hydrate shows different structures such as sI, sII, and sH, relying on the hydrate former. The gas hydrate as technology had been successful for several prospective applications in different engineering fields, for instance, gas separation, carbon dioxide sequestration, gas storage and transportation, energy source, refrigeration, and desalination of saltwater.

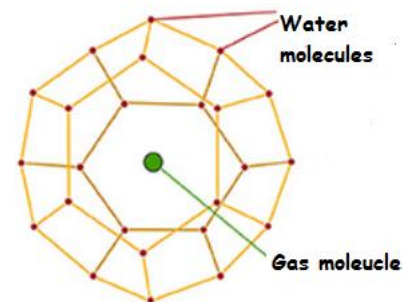


Figure 2 Gas Hydrate Structure

#### 3.1 Gas hydrate-based water desalination (GHBWD)

Gas hydrates are solid crystalline compounds consisting majority of water, a guest gas that can form hydrates at a comparatively lower temperature and higher-pressure conditions [29]. The stability of gas hydrate relies on the existence of hydrate former, the concentration of gas, and the existence of inhibitor or promoters [30-31]. Generally, hydrates are formed and stabilized, usually beyond the freezing temperature of the water. Overall, the formation of gas hydrate excludes all solids, dissolved species, and most organic species in the aqueous solution [32-34]. As pure water can only form hydrates, therefore, all the impurities like salts and others are easily separated and eliminated [35-38]. Once the gas hydrate dissociates, only gas and pure water are generated without any other impurities [23,34,39], which provide the basis for the desalination process through hydrate formation and dissociation. Salts dissolved in seawater have usually inhibiting influence on hydrate formation, and thus it requires substantially more degree of subcooling to form hydrate [16,40]. This limitation could

overcome easily by either addition of suitable guest gas i.e., propane, tetra hydro Ferron (THF), sodium dodecyl sulfate (SDS), cyclopentane, cyclohexane, SF<sub>6</sub>, and other refrigerants [25, 31-33,36 ,41-42].

### **3.2 Concept of hydrate-based water desalination process**

The hydrate-based water desalination process is established on the phenomena of phase change in which liquid water is altered into solid by sorting out the dissolved solids from the liquid water. The desalination process using the gas hydrate process requires hydrate former to be mixed with the produced water in a hydrate reactor, which is then followed by separation using hydrate formation in a crystallizer. The process flow sheet represented in Figure 3 explains the phenomena of hydrate-based water desalination. Initially, the reactor is pressurized by air or gas so that there is no residual air present in the reactor. Afterward, the desired volume of produced water was introduced into the reactor and wait until the system cooled down. The reactor is connected through guest gas from which gas is being supplied to the reactor. The produced water and the guest gas present inside the reactor is thoroughly mixed with the help of a stirrer, so that thorough mixing takes place to form gas hydrate by making a proper interface bonding between the water and hydrate former at the required pressure and temperature conditions. Lower temperature and the higher-pressure environment are maintained in the reactor for a given gas hydrate system. After the formation of hydrate slurry, it is then transferred to the crystallizer. This hydrate slurry is converted into a solid structure along with the concentrated brine. This concentrated brine is drained out from the crystallizer. Further, the crystalline solid structure of gas hydrate transferred to a decomposition chamber where the gas hydrate decomposes into gas and water by adding heat. The gas then flows into the gas storage tank through the upper portion of the decomposer, and the pure water is collected at the bottom, which can be used for the industrial and domestic areas. The pressure of the gas, temperature, reactor pressure, temperature, crystallizer, and separation are controlled through a proportional integral derivative (PID) controller, and data is fed into the acquisition system at frequent intervals.

When a highly saline mixture is in contact with a hydrate former at appropriate temperature and pressure, there would be a phase change from liquid to solid. The formation of hydrate eliminates ions as well as salts from the crystals. It is eminent that the existence of salts moves the hydrate phase equilibrium towards lower temperature and high pressure by showing its inhibition phenomena [43-49].

## **4. LITERATURE REVIEW**

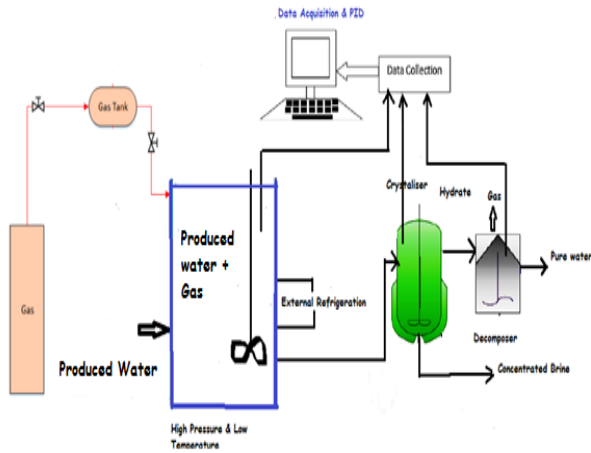
This segment lists and demonstrates the state-of-the-art developments within research related to treating produced water by hydrate-based water treatment process. Most of the

researchers reported that the gas hydrate-based water desalination process is subjected to a higher operating cost than the thermal and mechanical desalination process owing to higher pressures and lower temperatures required for hydrate formation. Nevertheless, hydrate formation is dependent on the type of guest molecule. One of the researcher precisely [32] stated that by introducing a secondary guest molecule, it would be capable of creating gas hydrate formation without much difficulty than pure gases since they offer more substantial stabilization energy to the hydrate structure [41,50,51]. Produced water along with (CO<sub>2</sub> + cyclopentane) and (CO<sub>2</sub>+ cyclohexane) hydrate formers showed an increase in temperature from -2 °C to 16 and 7 °C. The slight hydrate formation temperature and faster rate signified improved energy efficacy of the double hydrate for the gas hydrate-based water treatment system with a removal efficiency of 90%. Analysis of Ion concentration in treated water is determined as removal efficiency and is established as

$$\text{Removal Efficiency } (\eta) = \frac{C_{A0} - C_A}{C_{A0}} * 100 \quad (1)$$

Where  $C_{A0}$  concentration of ion present in produced water at inlet and  $C_A$  is the salinity of dissociated water. Fakharian et al. [52] carried out gas hydrate-based water desalination with two different produced water samples obtained from Iran along with compressed natural gas hydrate former to appraise its possibility. This study reported that to achieve greater removal efficiency of heavy metal numerous steps of hydrate formation is essential as most of the saltwater is confined between crystals of hydrate. This effect of the increase in hydrate formation is due to the memory effect in subsequent stages and also figured decrease in the total amount of dissolved solids. Formation of hydrate is performed at 95 bar and 274.2K and reported removal efficiency of 79-84.3% of dissolved minerals including cations, anions and indicated that hydrate-based water desalination could be realistic having initial TDS less than 160,000 ppm. In another study [53] reported regarding treating of different saline produced water samples along with pure CO<sub>2</sub> by implementing the gas hydrate-based water desalination at 35 bar and 273.2 K. It is concluded that by using a three-stage process 82-89.2% removal efficiency is attained.

In another instance, [54] investigated the effect of gas type and salinity by using CO<sub>2</sub> and natural gas. The hydrate formation experiments were done at 274.2K at 3.5, 9.5 MPa and reported a removal efficiency of 86% by using a three - stage process using CO<sub>2</sub> as hydrate former whereas desalination efficiency is figured to be 82 % by using natural gas which might be due to the framework assembly of CO<sub>2</sub> that is packed compared to natural gas. In order to improve the water recovery and kinetics of hydrate formation for the argon gas mixture, the effect of sodium dodecyl sulfate was evaluated under different concentrations of 100ppm, 500ppm, and 1000ppm, and figured that the addition of SDS of 500ppm did improve the kinetics and water recovery significantly with water recovery of 36% when operated at 55 bar, 274.4 K.



**Figure 3:** Schematic flowsheet of Gas hydrate-based water desalination process

By using CO<sub>2</sub> with 10 % propane gave a water recovery of 43% [55]. In the presence of low concentration of CH<sub>4</sub>, hydrate formation kinetics of CO<sub>2</sub> was reported. Stirring mechanism helped in removing heat from the reactor which resulted in higher yield as well as better gas consumption in both the batch process as well as stirred tank [56].

## 5. CONCLUSION

Desalination of produced water is an essential source of freshwater considering the fact of the shortage of fresh water. Intending to meet the rising water demand and in order to decrease the environmental impact of the petroleum sector it is menacing necessity to reuse produced water. Its reuse will try to diminish the stress on the availability of pure water to nations where population and economic development are increasing rapidly. This gas hydrate-based water desalination seems to be a promising technology based on the experiments performed as one mole of hydrate constitutes about 85 mole% water and 15 mole % hydrate former. In this work, we have reviewed state of the art in literature and listed the key contributions. The facts listed above conclude that hydrate-based water treatment is encouraging compared to conventional desalination methods in terms of energy- saving feasibility on a larger scale and as well as maintenance. With additional research and progress in identifying improved hydrate formers that can provide good driving force and advanced design hydrate-based, water desalination can become an economic and viable solution for treating produced water thereby providing reusable water.

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