Desalination of Seawater through Gas Hydrates

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Abstract— *Water is an elixir of life and was basis of human civilization. Rapid growth in population promotes consumption of freshwater due to more industrialization and urbanization. Hence, the demand of freshwater is being increased for agriculture, industrial and domestic sectors day by day. Moreover, per capita water availability is also decreasing from 5117 m^3/year in to 1371 m^3/year in 2025 (MWR, GOI 2019). Shortage of water lies in more than 80 countries and almost 40% population of the world facing this problem (Sabil et.al., 2013). As about 97 % of water existed on the planet earth as seawater (Brown, 2017) and it may be good alternative for fulfill the demand of freshwater after desalination. Desalination is the process of the removal of salts from the seawater using economical processes to convert them to fresh water. It is estimated that about over 75 million people worldwide obtain fresh water by desalinating seawater or brackish water (Khawajia et al., 2010). Therefore, many countries in the world are investing heavily in the seawater desalination for production of freshwater. The five world leading countries by desalination capacity are Saudi Arabia (17.4%), USA (16.2%), United Arab Emirates (14.7%), Spain (6.4%), and Kuwait (5.8%) (Khawajia et al., 2008). Among the different methods of seawater desalination (reverse osmosis and multi-stage flash distillation etc.), gas hydrate-based desalination technology is a relatively new one that has created an interest among the researchers and institutions (Sangwai et.al, 2013). Gas hydrates are crystalline solids made of the water (host) and the gas molecules (guest) such as methane, carbon dioxide, nitrogen, etc., which are held within water cavities that are composed of hydrogen-bonded water molecules (Babu et.al 2018). Process in gas hydrates-based desalination technology is depend upon the phase change of liquid to solid thereby removing the solids from the liquid phase. Economically gas hydrates-based desalination technology as compared to the conventional technologies such as reverse osmosis (RO) and multi stage flash (MSF) distillation looks a promising alternative for desalination of seawater (Park et al., 2011). As low temperature requirement is an important factor in gas hydrate formation process, implementation of gas hydrate desalination technology in the colder region would also enhance the economy of process by saving the energy cost for chilling the sea water. In future, the hydrate process can be made more economical by using some cheap and easily available hydrate formation promoter. Hence, the research in this direction is an ongoing process and may be very useful for fulfil the future demand of freshwater.*

Keywords— Desalination, Gas hydrates, Seawater.

I. INTRODUCTION

Many nations are experiencing fresh water crisis as a result of population increase and the tremendous development of industrial and agricultural operations. 1 in 6 of the people (approximately 1.2 billion) do not have enough access to safe drinking water, and the 1 out of 6 children dies for every 8 seconds after drinking polluted water. By 2025, 1.8 billion people will live in nations and territories with absolute water scarcity, and two-thirds of the world's population may face water scarcity. The management of water resources affects nearly every aspect of the economy, especially health, food production and safety, domestic water and sanitation, energy, industry and environmental sustainability. The future of water and energy resources is inextricably linked, requiring the development of innovative technologies to strengthen the water-energy relationship. Freshwater resources represent the total amount of water available on earth. The total freshwater supply available for ecosystems and humans is less than 1% of total freshwater resources. In recent decades, seawater has emerged as an important source of freshwater, as it is one of the most abundant resources on earth (97.5%) and a core technology for alleviating freshwater scarcity. MSF remains the dominant desalination technology in the Middle East, accounting for 50% of global consumption, due to the ready availability of fossil fuels and poor feed water quality. RO is the current state of the art for seawater desalination The RO process can treat feedwater within the TDS (Total Dissolved Solids) range of 10,000 to 60,000 mg/L. A typical seawater RO plant has a total water recovery of less than 55%. Total water recovery is the ratio of the amount of water produced to the amount of feed water The total energy required for RO is 3-6 kWh per m3 of recovered potable water. The biggest disadvantage of these methods is that they consume a lot of energy. The energy cost of meeting the expected global water demand with current technology is significant, particularly in a carbon-constrained society. Because water and energy. To meet the future demand for fresh water, there is a need to create novel technologies that may enhance the water-energy junction and increase the efficiency of existing thrust of freshwater. For seawater desalination, hydrate-based desalination has been suggested. The procedure essentially comes under the category of freezing or freeze desalination technologies. In the process water molecules create cages around a guest gas/liquid component in this mechanism, successfully isolating themselves from brine solution even at temperatures beyond the freezing point of water. When these hydrate crystals are melted, they become virtually fresh water, and the guest component may be reused in the desalination process. One mole of hydrate contains around 85% water and 15% guest gas, indicating that this technique has a great potential for creating reasonably pure water. The salt is only a thermodynamic inhibitor and is thus not allowed in the hydrate cages (Han *et.al.*,2017). The procedure has the benefit of using less energy because it runs at temperatures well above the freezing point of water.

II. MATERIAL AND METHOD

2.1 Hydrate based desalination

Hydrates are crystals consisting of hydrogen-bonded water molecules and guest (hydrate precursor) molecules contained within hydrogen-bonded cages. Hydrates can occur in liquid saltwater containing former (Precursor in table 1) in the form of solid phase when particular temperature and pressure conditions are met. The development of hydrate crystals is accompanied by the exclusion of dissolved ions and salts. The hydrate-based approach is closer to the freezing method among saltwater desalination technologies. The hydrate-based approach requires high pressure and low temperature to produce driving power, but the freezing method requires considerably lower temperature. As a result, judging them in terms of energy is difficult. It is said that the salts may become trapped in ice and be difficult to extract if the freezing rate is not very slow. As a result, further mechanical purification techniques like washing and centrifuging are still required after the freezing procedure. Researchers are likely to use a hydration-based approach to determine the key distinction between ice and hydrate as a result.

TABLE 1
TYPES OF FORMERS USED IN GAS HYDRATE DESALINATION (HERE, CP REPRESENTS CYCLOPENTANE AND R141B REPRESENTS CH3CCL2F (HCFC-R141B) ZHENG ET.AL.,2019)

Former types	Advantages	Disadvantages	Representative formers	Features
Gaseous	Easy to separate with water	High cost for pressurization	CO_2 C_3H_8	Non-toxic and accessible More moderate conditions but flammable
Gaseous + liquid	Lower cost for pressurization	Need to be separated furtherly	CO_2 + CP CO_2 + R141b	Insoluble and improve formation greatly Inexpensive with triple efficiency

When we compare some findings (table 2), we get better opinion about the gas hydrate-based desalination Recently, several researchers around the world have done this removal Efficiency Test of Hydrate-Based Desalination. 2012 cha Seol et., measured the removal efficiency of high salinity (9 wt.%) water that utilizes CO2 and insoluble hydrocarbons to form double hydrates in a stirred reactor thus achieved over 90% removal efficiency of salts (Na+, Mg2+, K+, and Ca2+) In the same year, Yu et al., conducted step-by-step demonstration of the CO2 hydrate desalination effect with brine solutions of different concentrations. they analyzed and investigated the relationship between initial salinity and residual salinity and suggested that residual salinity should be controlled below 4% by weight. In 2013, Liu et al., assumed multi-stage hydrate-based desalination using CO2 with the addition of CH3CCl2F (R141b). They observed the Improved removal of R141b (1:70 volume ratio with seawater) which gave the removal efficiency tripled, potentially increasing desalination rate that is the grade goes up, up to

98.4%. Later in 2014, Kang et al., analyzed and observed the removal characteristics of dissolved ions by squeezing gas hydrate pellet which resulted that there was no obvious difference was found (less than 1%) efficiency between cations and anions using CO2 as hydrate former. The removal efficiency of each ion using methane is relatively low than the applicable use of CO2. In 2017, Kang et al., used the same device to produce CO2 hydrate ICP-AES (Inductively Coupled Plasma) has confirmed a removal efficiency of over 75% of dissolved ions. Therefore, there is a great opportunity Hydrate-based desalination as a method of seawater treatment.

TABLE 2
MILESTONE OF RESEARCH PROGRESS OF HYDRATE-BASED DESALINATION

Year	Reference	Description
1942	Parker, A	Proposed application of hydrates for seawater desalination
1961	Knox *et.al.,*	Flowsheet and Material balance with propane as hydrate former was presented
1962	Barduhn *et.al.,*	Criteria for choice of good hydrate former was laid down
1964	Koppers Co	Two pilot plants were built at Wrightsville Beach with R-12 and Propane as hydrate former
1998	McCormack *et.al.,*	Pilot plants at Hawai and San Deigo were built by Thermal energy systems based on R141b as hydrate former
2008	Bradshaw *et.al.,*	Extensive kinetic as studies by Sandia National Laboratories employing HFC 32. R152a, R141b hydrate former
2011	Park *et.al.,*	A new apparatus with dual cylinder units producing CO_2 hydrate pellets was developed and demonstrated
2014	Babu *et al.,*	Fixed bed approach utilizing LNG cold energy was proposed

2.2 Process and water recovery

When saltwater or salt solution comes into contact with a hydrate-forming agent at the right temperature and pressure, a solid phase is created (clathrate or gas hydrate). Salts and dissolved ions are excluded from the hydrate crystals during the hydrate formation process. As a result, it provides a foundation for the separation of clean water from an electrolyte (salt) solution, such as seawater or brackish water. It should be noted that the temperature during formation might rise over the water's freezing point. Additionally, the brine and hydrate crystals can be mechanically separated. The hydrate crystals can be removed and then broken down by depressurization or heat stimulation. The water and the molecules that comprise the hydrate are released when the hydrate crystals dissociate. The latter is recyclable and recoverable.

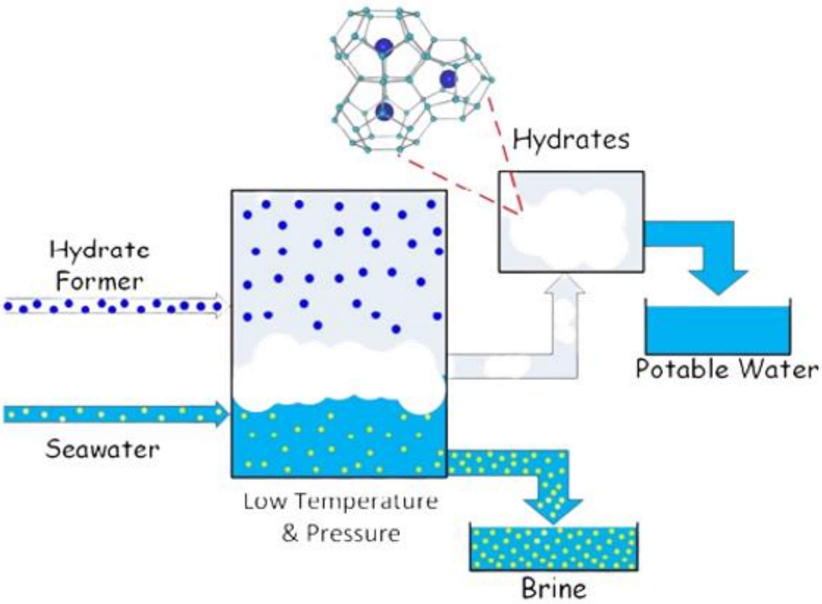

FIGURE 1: Block flow diagram illustrating the concept of hydrate-based desalination (Babu P *et.al.,* 2018)

III. RESULT AND DISCUSSION

The volumetric process effectiveness of hydrate-based desalination is represented by water recovery. The amount of water in the feed solution that is used in the process is transformed into hydrate. But often, fewer than 100% of the hydrate crystals are recovered. As a result, the percentage of the hydrate generated that can be recovered during the process of separating the hydrate crystals from the brine is used to determine the water recovery (%). To retrieve water, the collected hydrate from the hydrate/brine separation will be dissociated so the water recovery can be defined as the volume of water converted to hydrate to the volume of feed solution with consideration of fraction of hydrate formed will the percentage of water recovered from the total amount of water feed for desalination(Sadeq *et.al.*,2017) (Note: Here fraction/factor is the hydrate recovered which represent the separation efficiency of hydrate-based desalination process). Higher water recovery is seen if it results in the production of more hydrates and the efficient separation of hydrate crystals from brine (Lv *et.al.*,2018).

Although laboratory tests have demonstrated the viability of hydrate-based desalination, there are still two issues that must be resolved through innovation in the near future. One factor that significantly affects production costs is the choosing and operation of the hydrate forming. This requires thorough research on various former types, taking into account the phase state, solubility, safety, price, recycling, and other factors. Another factor that determines how effectively fresh water is removed is additional separation and purification.

IV. CONCLUSION

One of the most promising solutions to help with a growing water issue is desalination. The most common desalination process in use today, reverse osmosis requires a lot of energy. Therefore, to increase the energy-water confluence, revolutionary energy-efficient technology must be developed. One such method is hydrate-based desalination. this paper gives an overview of some emphasised process and general information regarding hydrates and the function of desalination technology, the technology has been explored over the past 70 years, but due to delayed hydrate formation kinetics, challenges in hydrate crystal separation from brine without contamination, and expensive refrigeration costs, it was never commercialised. Using a more inventive reactor design, better hydrate-forming agents, and other technological advancements can be formalized for better mitigating the upcoming water scarcity issues in the world.

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