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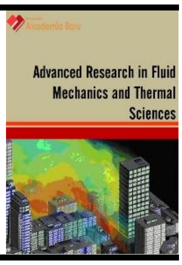


# Desalination of Seawater through Gas Hydrate Process: An Overview

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**ABSTRACT**

Potable water shortage affects more than 80 countries and 40% of the world population. It is predicted that over 60% of the human population would be exposed to water shortage by the end of 2020. Marine water represents an infinite water source since 98% of all global water is present in the form of oceans; therefore, seawater desalination is the most logical approach to meet freshwater demands. Currently, two dominant desalination methods are widely applicable includes reverse osmosis and multi-stage flash distillation. Although these technologies have been proven to be reasonably efficient, they still have some disadvantages, i.e., high capital investment or not feasible for minor scale. To overcome the limitations of the existing techniques, new technologies like Electro deionization (EDI), Freeze Separation (FS), Vacuum Compression Distillation (VCD) and Freezing with Hydrates (FH) must be seeking as future applications. Some recent researchers have highlighted the desalination with hydrates can produce cheaper desalted water than the existing available technologies. This study provides a brief review of the recent researches accomplished on the desalination of saline water through gas hydrate technology. It is evident from the literature that small amount of additives or hydrate promoters either significantly enhance the thermodynamic conditions of hydrate formation above the freezing point of water or increase the hydrate crystallization by improving the hydrate formation rates. This review paper will provide the roadmap for the potential application of hydrate technology in the field of water desalination.

***Keywords:***
Desalination, Freshwater, Gas hydrate, Hydrate desalination, Promoter



## 1. Introduction

Water is vital for life, not only for daily human consumption and supporting ecosystem but also for agriculture and industrial uses [1-4]. It is proven the fact that the annual precipitation on earth is adequate for the need of the earth's population; however, its distribution is not uniform. In many parts of the world which have limited or no water resources, rainfall is almost nonexistent [4,5]. Many

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areas around the world such as the Middle East, Northern China, North Africa, and the middle and western parts of the USA are considered to be impoverished water area. Shortage of water lies in more than 80 countries and almost 40% population of the world facing this problem [5]. Approximately over one billion people live where water is economically scared or places where people lack the infrastructure to utilize water efficiently and make this water available. Moreover, in some places around the world, due to the uncontrolled increase in population, deteriorated water quality led to water scarcity as well [6,7]. Due to the seriousness of this issue, government agencies, local, regional and international bodies have been developing programs to search for new water sources and simultaneously creating policies that limiting the quantity of water demand to integrate the current resources along with population growth and industrial expansion [5].

The oceans perceived as the world's genuine water depository. Around 97% of the world's water lies in the form of seawater while an additional 2% secured in the form of ice caps and icy masses. Accessible freshwater reserves actually below 0.5% of the world's cumulative water resource [4]. Massive portions of the freshwater trigger the world's surface. However, a lot of them are too profound to access in a commercially proficient way.

Moreover, seawater is unsatisfactory for human utilization, industrial and farming engagements due to the presence of a total dissolved solids (TDS) level of seawater ranges from 3000 mg/L to 4000 mg/L [1,5]. The mineral content is too high that it is impossible to be used directly in any human activities. Therefore, seawater assassination is the logical process to be explored to meet raising freshwater demand by tapping into abundant seawater resources. Desalination can be defined as; any process that removes salts from water or reclaimed water into potable water by removing salts and other minerals. The key ions present in seawater include $Na^+$, $K^+$, $Ca^{++}$, $Mg^{++}$, $Cl^-$ and $(S0_4)^-$, and of course, all additional ions found in the environment, but at far lesser concentrations [4]. The process is not new since Greek sailors were used to desalinating water by evaporating it as early as the fourth century. Infect, Aristotle observed the principle of distillation through the desalination process during that era. In the year 1869, the first patent for desalination process had been reported, and the first desalination facility was established on the island of Curacao in the Netherlands Antilles in 1928 followed by a major desalination plant in Saudi Arabia ten years after [4]. However significant development in desalination technologies has started during World War II to provide fresh drinking water to the military establishment in arid areas [3]. Currently, the two major desalination processes are multi-stage flash (MSF) and reverse osmosis (RO) methods [4,8,9,15].

Desalination is enormously important to many countries for a freshwater generation. Today, a few nations rely on desalination advances with the end goal of meeting their higher water prerequisites. Specifically, in the Middle East, seawater desalination is a key method to get the fresh water in countries like Kuwait, Saudi Arabia and the United Arab Emirates [5]. Moreover, it is likely that desalination will keep on developing its reputation in the Middle East [5]. Generally speaking, it has evaluated that more than 75 million individuals overall get fresh water by desalinating seawater. The IDA Desalting Inventory report [1] demonstrates that, toward the end of 2002, introduced and contracted brackish (saline) and seawater desalination plants overall totalled 17,348 units in 10,350 desalination plants with an aggregate limit of 37.75 million $m^3$/day of fresh water. The five world driving nations by desalination limit are Saudi Arabia (17.4%), USA (16.2%), the United Arab Emirates (14.7%), Spain (6.4%), and Kuwait (5.8%) [10,11].

## 2. Different Types of Desalination Methods

Numerous kinds of water desalination routes have developed in recent times for continual improvement. Figure 1 demonstrates the various types of desalination processes. Principally, the desalination methods can be categorized into the following two classes: single phase (membrane processes) and phase change (thermal processes) [7,12]. In the single-phase routes, membranes are widely employed for the desalination of saline water. Their prime examples are commercially important desalination processes like Electro Dialysis (ED) [1,5,13] and Reverse Osmosis (RO) processes [1,12,14–16]. Phase change routes require a thermal energy source, for instance, fossil fuels, solar energy, or nuclear energy perhaps used for vaporization of saline water (evaporation), which subsequently condensed to acquire fresh water. Multi-Stage Flash (MSF) distillation [3,4,12,17], Solar distiller [3,7], Vapor Compression (VC) distillation [1,7,8], Multi-Effect (ME) distillation [7], Ultrafiltration (UF) membranes [18–22] and crystallization (Hydrate Freezing) [17,23,24] processes are the prime examples of desalination through phase change method.

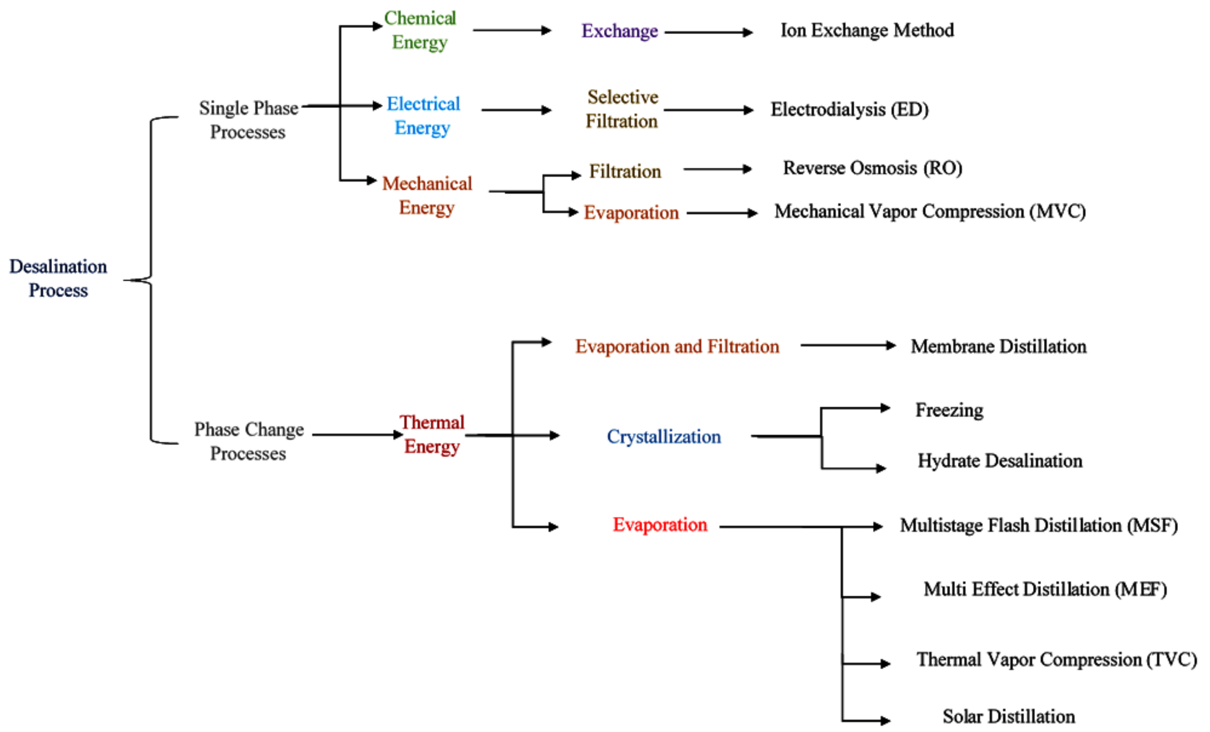


**Fig. 1.** Various Desalination Techniques for removal of salts from Seawater

Although these technologies have been proven to be reasonably efficient, they still have some disadvantages. For example, RO requires substantial capital investment and maintenance, whereas MSF is moreover energy intensive process [8,12]. Besides, neither of the processes are capable of removing all the impurities from saline-water or contaminated source; and they must discharge up to 50% of their input as concentrate [25]. Besides, these technologies are expensive for small volume production, which make them inappropriate for rural areas applications [26]. To address the above mentioned limitations, new technologies must be explored for the efficient and economically feasible solutions. Several innovative methods have investigated with impending for future desalination applications [3]. For instance, electro-deionization (EDI) is a combination of electrodialysis and ion exchange process. Other novel technologies include membrane, or combinations of membrane/ distillation, and freezing with gas hydrates. Among those, gas hydrates seem to be a very clear option to be explored as the future desalination technology [1,27–29]. The use of gas hydrates in the desalination process is attractive because gas hydrates will form from seawater such that salt ions are excluded [17,24,30–32]. In the year 2011, Park *et al.,* [33], reported that through their new reactor they were able to produce potable water through gas hydrate technology 50% cheaper than current technology. Furthermore, it has also been reported by Javanmardi *et al.,* [34], that desalinating of highly salty water through gas hydrate technology is consumed lower energy usage combined with the further advantage of avoiding pretreatment processes.

## 3. Overview and Historical Perspective of Gas Hydrates

Clathrate hydrate also abbreviated as "hydrates" are solid crystalline inclusion compounds of water (majority species) and a guest molecule (minor species) that form at a relatively low temperature and high-pressure conditions [35–40]. The region where gas hydrates are stable is known as gas hydrate stability region, and it depends on the presence of a guest molecule, the concentration of each gas (i.e., natural gas) and the presence of inhibitor or promoters [28,41–46]. The hydrates are formed and stabilized usually stable above the freezing temperature of water, though the addition of some large molecule guest molecules could maintain hydrates at nearly ambient temperature. In general, the formation of gas hydrate excludes all solids, dissolved species and most organic species in the aqueous solution [23,31,32]. Since only pure water can form hydrates, therefore, all the impurities like salts and other are easily separated and eliminated [17], [33,47,48]. When the gas hydrate dissociates, only gas and purified water are produced without any other impurities [24,30–32] which provide the basis for desalination process through gas hydrate formation and dissociation. Salts dissolved in the seawater have a natural inhibiting influence on hydrate formation, and thus it has required substantially more degree of subcooling to form hydrate [4,49]. This limitation can be overcome easily by either addition of suitable guest gas i.e., propane ( $C_3H_8$) or insertion of appropriate hydrate promotors like Tetra hydra Ferron (THF) or Sodium dodecyl Sulphate (SDS) [29,41,43,44,50–52].

## 4. Desalination of Seawater by Gas Hydrate Based Technology

The use of a clathrate hydrate-forming agent or hydrate promoters was started as early as 1960's by some groups to facilitate the freeze distillation of saline water. Koppers Co. initially established the desalination method based on propane hydrate formation. Sweetwater Co. was another company which adopted the hydrate desalination process initially. Both companies operated pilot plants services with the provision of the office of saline water US [53]. Barduhn *et al.,* [54–57], had explored a range of hydrates formers to studied kinetic and hydrate separation in a continues flow system. In the next decade between 1960 to1970, numerous process outlines were established and demonstrated at pilot scales level. This was due to the struggle of separating hydrate crystals from the concentrated brine and the deletion of dissolved hydrate former gas (guest) from the recovered water (host) [1,30]. Earlier, the Hydrochlorofluorocarbon (HCFC) refrigerant (R141b) was directly injected into a pressurized reservoir of seawater at hydrate forming condition (100 psi and 5$^{o}$C) by the Bureau of Reclamation commissioned through Thermal Energy system, Inc., at San Diego and Hawaii, USA [10,11,58,59]. Produced complex suspension of hydrates and brine (slurry), of which gas hydrates must be recovered and separated from the seawater before dissociation. In this processes, the hydrates crystals formed were small and dendritic with a high amount of salt trapped in the interstitial spaces. The test was fairly useful, though a wash column was not constructed and tested as part of the process [10,11,58,59]. The estimated cost of the operation was between \$0.59-0.68/m$^3$ and \$0.46-0.52/m$^3$ respectively. These studies highlighted the operational problems involved and further improvement required for the desalination process through hydrate formation which include the difficulty in separating the gas hydrate and salt crystals. It also highlighted the importance of determination of filterability of hydrate crystals, the plan and operation of wash column and hydrate formers (promoters) that allow the processes to be operated relatively lower pressure and higher temperature conditions [2,3].

Englezos and Ngan [60] investigated the recovery of water from pulp plant effluents with 2.5 wt.% NaCl solutions in the presence of propane gas [36]. They found that 31% reduction in the salt contents of the recovered water. Alieve *et al.,* [24], studied the conditions for the efficient hydrate formation in the system constituted by twice-distilled water and the Freon 142-V chemical. They reported that the raising of stirring rate from 20 to 1350 rpm besides reducing the bubble diameter from 3.0-3.5 to 0.5-1 mm results in intensification of the hydrate formation. Bradshaw *et al.,* [61], provided the molecular picture of the structure and dynamics of R141b (guest molecules) within water cages (host), acquired from molecular dynamics simulations and Raman spectroscopic method. To solve separation difficulty between brine solutions and hydrate crystals; Parks *et al.,*[33], designed equipment to quickly separate dehydrated high-density gas hydrates from hydrate slurries. Jong-Ho Cha and Yongkoo Seol [23] determines the importance of co-guest gas like cyclohexane (CH) and cyclopentane (CP) significantly enhanced the $CO_2$ hydrate formation temperature from -2$^{o}$C to 6-7$^{o}$C. Additionally, the kinetic study revealed that mixed gasses increase the hydrate formation rates for the dual hydrates through CH and CP are shown to be 16 and 22 times greater than the pure $CO_2$ hydrate with purity of 90% salt removal efficiency also attained [23].

The Economic aspect of the hydrate desalination is precisely a significant cause for investigating the feasibility of the method along with research exploration [4,5]. According to Javanmardi and Moshfeghian [34], the operational budget of hydrate-based desalination technology driven by numerous issues such as the presence of salt content, seawater temperature, the mobility of salt and yield obtained. Park *et al.,* [33], highlighted that the removal efficiency of hydrate desalination is likewise be governed by on ionic charge and ionic radius of the cation exist in the form of the mineral. The effectiveness of the desalination process decreased with high ionic charge while larger ionic radius significantly increased the desalination efficiency [33].

### *4.1 Process Description*

From the discussion of the previous section, it can easily be concluded that; gas hydrate-based desalination method has been measured as an attractive alternative to reverse osmosis or conventional distillation methods [1,24,30,33,47,59]. Subsequently, the structure of gas hydrates embraces only gaseous (guest) and water molecules (host), therefore, the formation of hydrates excludes entire impurities (salts or other) from the crystalline structure and exodus them in the form of residual saline water [10,24,26,31]. Underprivileged experimental data are available on the hydrate desalination process. Considering the writing, overview conveyed as such, a procedure for desalination utilizing hydrates as appeared as a part of Figure 2. Sangwai *et al.,* [14], already describe the desalination process using gas hydrate method depends on the phase change process. Wherein, the liquid water turned into stable hydrate by separating the broke up solids from the liquid stage. The desalination process utilizing hydrate innovation need hydrate former or guest molecule, for example, gas to be mix with the salted water, which is then trailed by division using hydrate formation. To enhance the hydrate formation rate various researcher employed hydrate promoters to facilitate hydrate formation [12,17,24,61]. Overall process flow sheet of the hydrate-based desalination technique is illustrated in Figure 2 portrays the strategy of desalination of seawater through the gas hydrate technique. Before entering the seawater into the hydrate reactor, the heat of water is pulled up through the heat exchanger.

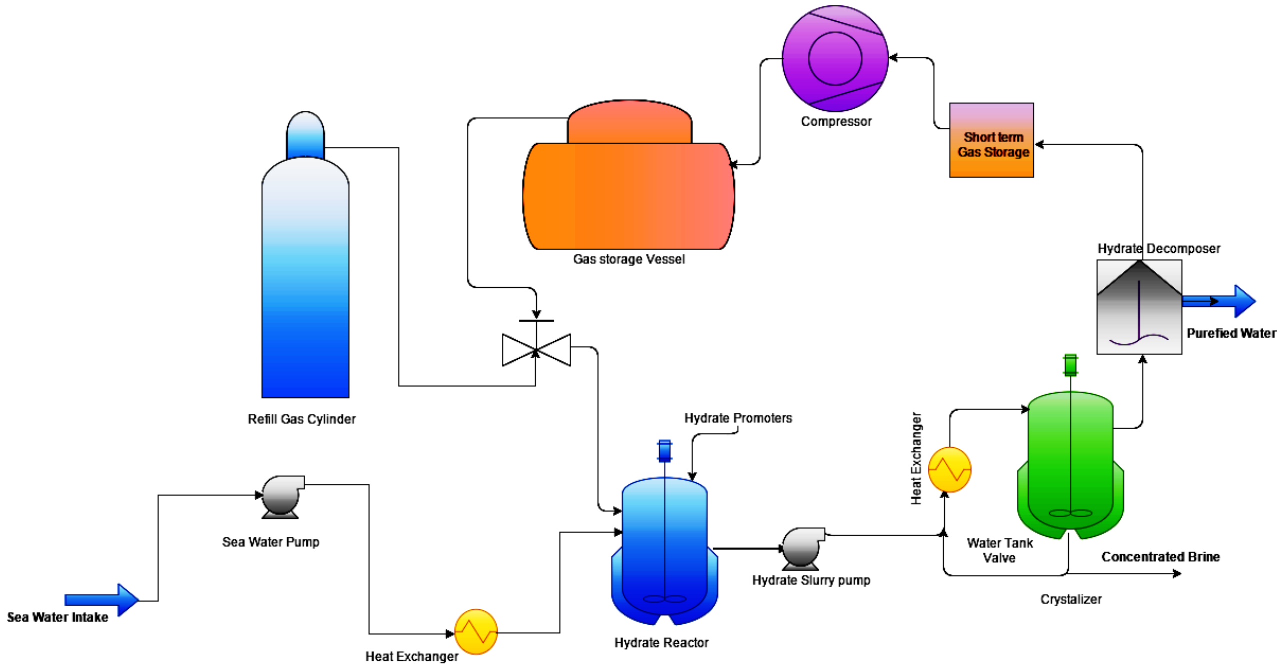


**Fig. 2.** An illustrative flow sheet method for desalination through gas hydrate technology

The reactor can join with visitor gas chamber from which gas is being supplied to the hydrate reactor. Nevertheless, a make-up gas cylinder is accommodated conquering the gas losses amid process stream. The seawater, the visitor gas which is available inside the reactor and hydrate promoters are altogether blended with the assistance of a stirrer at a desirable RPM for thorough mixing to frame gas hydrate a spurious interface holding between the water and gas atoms at a required temperature and pressure conditions. Low temperature and high pressure conditions are kept up in the reactor for given gas hydrate structures. The addition of small quantities of hydrate promoters significantly lowered the interfacial tension between water and gas phase and provide further enhancement during hydrate formation. Subsequently, the newly formed hydrate slurry is then substituted to the crystallizer using a hydrate slurry pump. Then hydrate slurry is changed over into a crystalline solid hydrate structure alongside the concentrated brine solution as a residue. This concentrated brine solution is then coming out of the crystallizer.

Further the crystalline solid structure of gas hydrate switches over to a decomposer where again the gas hydrate disintegrates into gas and water by the dissociation of heat. The gas then streams into the short-term gas stockpiling tank through the upper part of the decomposer and the remaining water is gathered at the base, which can be utilized as a part of the mechanical and household zones for day by day schedules. Additionally, recycle gas again pressurized through the compressor and reuse over again.

According to Babu *et al.,* [31], it is possible to attain considerably higher water recovery range (60–80%) in 1 h operating time at less than 60 bars (6 MPa) from their unique sand bed reactor. Additionally, via application of propane gas as co-guest in various concentration along with the other constituents of the gas mixture; it is likely possible to attain higher conversions rates. Additionally by the addition of hydrate promoters like Acetone or others [51,62,63] to curtail the operating pressure for the desalination of hydrates. However, Desalination through hydrate is a future technology, and its conceptual process is presently one of the active investigation areas of research.

## 5. Conclusion and Recommendations

Desalination of seawater is an ultimate source of fresh water, almost 50% of the world population currently facing hindrance for getting fresh water. In this short review, the various emerging desalination technologies are discussed with a major focus on hydrate-based desalination technology. Desalination of saline water through Hydrate requires lesser energy requirements alongside the economical aspect of plant based on hydrate desalination technology, especially for remote areas. The facts above effectively concluded that hydrate-based desalination method stares as encouraging alternate paralleled to the conventional methods, e.g. multi-stage flash (MSF) and reverse osmosis (RO). Desalination application in the cooler region would also augment the economy of hydrate-based technology; by saving the energy cost for chilling the sea water since lower temperature condition has a significant influence on the formation of gas hydrate. Additionally, economical and readily available hydrate promoters along with co-guest insertion are currently a novel research area to make hydrate desalination cheaper and easier for commercial applications.

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