

# Application of Gas Hydrate Based Technique in Wastewater Treatment - A Mini Review

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## ABSTRACT

Worldwide economic growth, professional and domestic lifestyle and the ecosystem are affected by a lack of fresh water supplies. Oceans are the 97% part of earth's crust, due to increasing demand of growing industrialization and population it has become an important source of freshwater over the last few decades. Desalination is the core technology for mitigating the water scarcity problem by reduction of seawater salt via different removal techniques. The gas hydrate-based desalination and wastewater treatment are the impending techniques which not only can handle wastes but also provide an economic, less toxic and feasible purified water. Since isolation from wastewater, solid crystals produce pure water. In this work, a brief review of the literature estimated.

**Keywords:** Gas hydrate, heavy metal ions, wastewater treatment

## 1. INTRODUCTION

An ongoing threat for all the living species more specifically for humans is the scarcity of freshwater. Even large city centres, including places historically perceived to be waterways like Japan, face a shortage of water [1]. To overcome the problem of water shortfall on the planet, there is a need for recycling of water resources and the wise usage of wastewater from the industries and from the greywater production to provide drinking and non-drinking water. The water supply in premises may be constructively built to be reusable with the help of an efficient wastewater treatment facility installed into buildings and industry. Although water appears to be a limitless natural resource, the facts and figures published by various researchers indicate that just 0.5% of freshwater is safe for usage out of 326 million mi<sup>3</sup> on the planet [3]. Most freshwater is confined to glaciers in specific areas and relies on periodic climate changes. Due to abruptly increasing development of industries and population demands, water becomes a "stressed" resource. In 2019 UNESCO reported that, the global water demand is expected to continue to increase, allowing for an expansion of more than 20 to 30 per cent over the current water use in 2050[2]. There are three types of physical water scarcity: a) fewer than 25 per cent, b) between 25 and 70 per cent, and c) greater than 70 per cent. The areas in the Middle East and North Africa, like Central Asia, have a lack of physical resources of more than 70%.

In contrast, those in Asia and Central America are between 25 and 70% shortages of resources [2]. In studies by Hamad Yoonus et al. neglect economic poverty because of the lack of facilities for processing, shipping and water treatment for usage in regions [4]. At least once per month in a year, almost two-thirds of the world's people suffer from extreme

water shortages [5]. When water demand increases exponentially, policymakers may make an impact on the implementation of sustainable water management techniques.

The ocean is the overt source of the actual depository of water in the world. Around 97% of the world's water is seawater, while ice caps and frozen masses constitute a mere two per cent. Accessible supplies of freshwater below 0.5% of the total global resource for water [6]. The surface of the earth is caused by huge pieces of freshwater. However, several of them are too deep to be reached commercially.

Desalination technology is the salt removal method for seawater or brackish water, and it is known to be the freshwater depletion alleviation. In the last couple of decades, a significant development in coastal and brackish water desalination technology (disposable in freshwater and underground aquifers) has been made [7]. Conventionally and commercially, there are two types of treatment processes single stage (membrane processes) and phase change (thermal processes) [8]. Membranes are commonly used in single-phase routes for the disposal of seawater or pollutants with dirty water. Their key examples include processes such as reverse osmosis (RO) processes, which are economically and commercially developed worldwide [9]. In this treatment method, the semi-permeable membrane employed the concentration gradient to separate the solvent [10]. Phase Thermal change methods required thermal energy for vaporizing the wastewater, and in the case of ocean water, it is carried out by evaporation; subsequently, it is condensed to collect purified and freshwater.

Overall, such technologies are highly efficient, but each desalination technology has its intrinsic drawbacks. [11]. RO needs major pre- and post-treatments and membranes are capable of being fouled by oversized particles [38]

Contrary to this, multi-stage flash (MSF) processes need thermal and mechanical resources and are energy intensive [10][35]. Alternative desalination methods for reliable and cost-effective applications must be investigated to overcome these problems. Among these, the usage of gas hydrate as a potential treatment method tends to be an excellent choice.

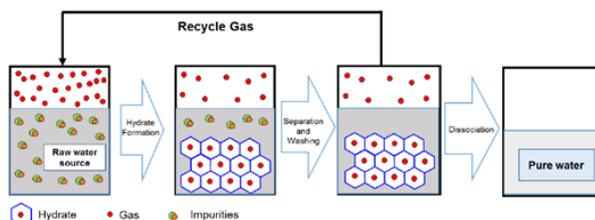
### 1.1 Introduction to Gas Hydrates

Nonstoichiometric crystalline complex of gas hydrate is formed by incorporating a guest molecule of the appropriate size and type in the lattice of the guest molecule, made up of hydrogen-bound water molecules [12]. The host molecules within the cage interact physically with the water molecules by Van der Waal energy. With thermal stimulation/depressurization and each, the hydrates melt quickly. Naturally, gas hydrate is found in permafrost and marine sediments, and it is considered as the greatest potential energy assets for the future.

Two recent articles discussed the various forms of gas hydrate deposits and the prospects for renewable gas output from these deposits [13] [14].

### 1.2 Concept of Gas Hydrate based Wastewater Treatment

In the hydrate-based water treatment method for solid-liquid separation, the water molecules form a cage-like structure around the guest molecule thereby efficiently separating them from brine solution at higher temperatures than the ordinary freezing temperature of the water. The crystals are primarily made up of fresh waters which may, and the guest molecule can be recycled upon melting of the hydrate crystals [15]. As seen Figure 1, The following measures involve the hydrate-based water treatment process : (i) formation of gas hydrates, (ii) separation of hydrates (iii) post-treatment to improve quality of water (e.g., washing, centrifuging), and (iv) hydrate dissociation to produce treated water and reuse of gas [17].



**Figure 1** A concept for water treatments via gas hydrate process [17]

### 1.3 Evaluation of Gas Hydrate based separation

Several scientists worldwide have researched gas hydrogen-based wastewater desalination and treatment with substantial attempts to investigate optimum kinetics, phase equilibrium and device process flow diagrams. Gas hydrate

formation is a slow process and could be expedited by using a hydrate formation promotor. Propane and refrigerant (R-12 or  $CCl_2F_2$ ) are the among other hydrate types. A laboratory-scale device of water recovery from a paper industry discharge showed the usage of propane to extract the hydrate and then detach hydrate crystals from the crystallizer without transferring the hydrates in another vessel. The method was also employed for the desalination of water, and a decrease in salt in 31% from the 2.5-wt NaCl solution was recorded. It has been found that agricultural water standards are not as ideal as freshwater standard.

The Barduhn Community in the 1960s proposed guidelines for choosing former gas hydrate for seawater desalination [29]. An appropriate gas hydrate formerly built for seawater desalination shall have an intermediate temperature range of 5.6 to 29.4 ° C, compliant with normal products, usable commercially and liquid at the required operating temperature/pressures. It shall be environmentally safe, non-flammable, solid, class II former hydrate, low price. Eight hydrate formers (Freon -31, Freon 152a, Freon 22B1, Freon 12B1, Freon 12B2, Freon 142b, vinyl chloride and cyclopropane) have been selected, based on the above parameters. The process economics of the hydrate formation depends on the intelligent choice of hydrate former. For thermodynamic phase equilibrium data from Freon 21, Freon 31 and methyl bromide with NaCl solution and seawater was reported. After the discovery of the hazardous nature of chlorofluorocarbons (CFCs), which are supplemented by hydrofluorocarbons (HFCs) as the effect of these have been prohibited because of their impacts on ozone depletion.

A method of hydrochlorofluorocarbon desalination by R141b, refrigerant hydrochlorofluorocarbons, was suggested by Thermal Energy Systems in the pipeline of seawater from ocean depths of 2000 ft. The formulated gas hydrate was engineered, and the surface salt scrubbed in transit while transporting to the surface of the earth. It has also been proposed that carbon dioxide be used as the hydrate former gas. At the seabed condition 2000 feet underwater at the pressure of 6.0 MPa. Hydrates can be produced at 4.0 MPa at 5.6 ° C with carbon dioxide. The drawbacks of this method were the high pumping gas costs at required depths, high dissolution of  $CO_2$  into the ocean water and upon dissociation of gas hydrates release of the high amount of  $CO_2$  in the atmosphere which increase the  $CO_2$  emissions. Thermal Energy Systems built pilot plants in Hawaii and San Diego. A pressurized, cold seawater reactor was pumped with the refrigerant R141b at 5.6 ° C, which created a complicated slurry of hydrates and brine. Salt was captured in the interstitial pores of the small and compact hydrate crystals and a filtration system and washing equipment were used to remove the captured salt from the hydrate crystals. Based on the above procedure, the costs of processed water were calculated to be \$0.46-\$0.52 per  $m^3$ , equivalent to RO (\$0.45-\$0.92 /  $m^3$ ) and MSF (\$1.10-\$1.50 /  $m^3$ ). Though washing provided drinking water with TDS quality specifications, the washing phase affected overall process performance, as part of the water created was used while washing the hydrate crystals for salt collection.

Wide-ranging experimental experiments have been carried out at the Sandia National Laboratories with a brief explanation of the general block flow diagram of a desalination mechanism to determine the rate of forming of hydrate and separation of hydrate crystals from salt brine by various hydrate types. R141b, HFC-32 (difluoro-methane), R152a (difluoroethane) and ethylene were the different hydrate formers used. A rate equation was developed and used for scale-up calculations based on training data. HFCs are mainly water-insoluble, and thus their kinetics of hydrate formation is very sluggish. HCFCs and HFCs are both highly effective greenhouse gases, and their use is steadily reduced worldwide. HCFCs and HFCs are inappropriate for the setting and thus are not appropriate for the HyDesal phase hydrate formers [27].

As an alternate hydrate former in the HyDesal method, Cyclopentane was suggested as an immiscible hydrate at a temperature of almost 8 °C in water and forms structure II and atmospheric pressures. In a stirred tank reactor, three wt. per cent of NaCl solution was tested for hydrate development and salt removal performance at an alternating stage of subcooling. The efficiency of the removal of NaCl of 70%–90% and the retrieval of water of 35%–40% were recorded. Various secondary treatment methods following cyclopentane hydrate formation were used to increase the performance of salt removal. Secondary procedures were used to rinse, wipe, centrifugate or sweat. Centrifugation resulted in 96% of the salt removal effectiveness, while 93 and 95% of the salt extracted were washed and sweated. Centrifugation is a costly and energy-intensive method and thus is not ideal for large-scale applications. The sweating period effect on the efficacy of salt removal has also been documented. The quality of salt removal improved by 97%. In the washing phase, the performance of salt removal was tested with different ratios of freshwater to feed water. It has been concluded that the gas hydrate desalination will guarantee an efficient washing process with 3% freshwater to feedwater ratio. The effectiveness of salt removal reduces as water is converted to hydrate. Washing method productivity is decreased by utilizing part of the water generated for washing. It is, however, recognized that the use of Cyclopentane has drawbacks. It is inflammable, emulsifies during dissociation, and after decomposition by hydrate requires a secondary separation from the generated water. A novel method has been described which can continuously produce carbon dioxide hydrate and create hydrate pellets. The system contains a hydrate reactor with a dual cylindrical tank, water and a gas feed tube, a bubble generator circulating device and a hydrate discharge unit. By compressing the hydrate slurry with dual-piston cylinders, the hydrate pellets were produced. This system will overcome the problem of hydrate crystal separation from brine. In a single-stage hydrate forming phase, a salt removal of 80% was observed with this unit. The findings revealed that the removal of ions depends on the ion size and its radius. In a single-stage process without pretreatment with CO<sub>2</sub>, about 71–94 per cent of any cation in the order of  $K > Na > Na^{2+} > B^{3+}$  and 73–83% of each anion is rejected. When the salt on the pellet surface was washed out, the quality of the process was improved.

Although the equipment can remove salts expeditiously, it needs energy for gas/liquid mixing in the bubble generator and for the operation of dual cylinders with the piston to pelletize the hydrate slurry. Advanced hydrate formulation kinetics in a silica sand fixed bed reactor, where the hydrate consists of propane as a co-guest, has recently been published. Kinetic studies at the microscopic level have shown that propane can attract scattered silica sand water for hydrate development in the gas phase.

Most research literature has centered on the discovery of an optimal hydrate to boost the kinetics of the production of the hydrate. Hydrofluorocarbons, hydrofluorocarbons, SF<sub>6</sub>, Cyclopentane, cyclohexane is used for hydrate formation purposes. A superior hydrate was not found amid all the attempts. Methane and CO<sub>2</sub> are greenhouse gases and would damage the climate if emitted into the atmosphere. The use of CFCs has been reduced because of their ozone depletion nature. Hydrofluorocarbons (HFCs) were substituted for CFCs. HFCs are scarcely soluble in water and are very sluggish to form hydrate. Cyclopentane and cyclohexane are toxic and highly volatile in nature.

Besides, the problem aroused with liquid promotor is that it needed separate treatment for removal. Several reactor configurations such as swirling, bubbling, spray sheets, a firm sheet with silica powder, glass beads and variable reactor configurations were used to boost the kinetics of hydrogen production by growing the interfacial gas-liquid contact field. Secondary treatment methods have been indicated to extract salt, adsorbed to the surfaces of the hydrate crystals, after hydrate forming, such as cleaning, centrifugation etc. These secondary processes influence the feasibility and economy of the method [25].

#### ***1.4 Recent Advances in Gas Hydrate Based Technology***

Wastewater produced from both industrial and domestic sources carries several toxic materials. The same strategy can be used for wastewater treatment, as employed the for desalination of seawater or brackish water. Wastewater containing heavy metals can pollute water and soil and thus should be handled and well treated before release in large bodies of water [18]. Though chemical precipitation and coagulation techniques for wastewater treatment have been used extensively, there are many limitations to these techniques [19][20][37]. Such parameters of raw wastewater (such as pH, form and volume of contaminants, temperature, etc.) may follow strict criteria for the implementation of these technologies. Therefore, alternate management approaches for pollutants containing heavy metals are progressively required.

There is a growing demand for alternative treatment approaches for heavy-metal effluent, which tend to be promising for hydrate-based separation. The scientific attention has been drawn by correlational experiments in the separation and purification, by employing gas the hydrate. The purification of seawater by using gas hydrate-based technique was reported back in 1942, which recently attracted more attention of the scientists. A relatively

reducing interstitial water chlorinities in deep-water hydrate sedimentary parts and noted that hydrate removes almost all the salt ions from the crystal structure, which forms the theoretical basis for hydrate-based removal of mixtures. Then a suggested desalination method for the manufacture of potable water and a pilot plant was set up to research the gas hydrate technology [22][36]. A suggested method to create filtered solute from a water-solute mixture [23][30]. Accurate evidence for hydrate formation from experiments and thermodynamic simulation in an analysis performed in research. This data may be used to improve wastewater treatment and hydrate desalination processes [24][25][31]. Huang et al. have analyzed fruit, citrus and potato juice concentrations using methyl bromide, trichlorofluoromethane, and 1,1-difluoroethane to remove organic mixtures and have suggested that the process eliminated 80% of the water content.

Furthermore, scientists reported another method for the treatment of Ni<sup>2+</sup> containing wastewater. The results of reaction time, water recovery, enrichment factor of Ni<sup>2+</sup>, desalination efficiency and multi-stage treatment have been reported. This study demonstrates that Ni<sup>2+</sup> containing wastewater is effectively processed with the hydrate-based technique. Cyclopentane hydrate produced at 2 °C in NiCl<sub>2</sub> solution with a Ni<sup>2+</sup> concentration from 20-1000 mg/L. The recovery of water can be as large as 43% with a process efficiency of 62-88%. By employing multi-stage hydrate reaction, the quality and efficiency of the purified water can be further improved to 99% [28][40].

## 2. CONCLUSION

Widespread applications for seawater desalination, wastewater treatment, and heavy metal processing can be included in the proposed hydrate-based technology. Gas hydrate technology is one of the promising innovations for addressing the emerging water crisis. While reverse osmosis is the world's most popular technology for water treatment, it is energy intensive. In order to improve the energy-water network, advanced energy-efficient technologies need to be created. In this report, the main technological achievements have been briefly reported and highlighted.

Although it has been researched for the last seven decades, gas hydrate technique has never been marketed because of slow hydrate forming kinetics, difficulty in the separation of hydrate crystals from residue and high higher refrigeration costs. With further systematic investigation and development to identify better hydrate promoters, innovative reactor design, it can be a sustainable solution for desalination and wastewater treatment.

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