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Freezing Separation Technology for Deawater Desalination Industry: Review Analysis and New Hybrid Process Proposition

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The paper explores the freezing separation process for seawater desalination purposes. Recent developments and innovations occurring in the freezing separation process are presented. Moreover, the main methods currently being investigated in this process, especially for seawater desalination, are reviewed and discussed. Finally, the possibility to use hybrid process, currently having significant profits, is exploited in order to propose and develop new innovative seawater desalination system. As a result of this study and analysis, a hybrid process that is consisting of combining freezing technology upstream reverse osmosis (RO) module for seawater desalination was suggested.

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Introduction

In this modern century, the lack of potable water is still a problem in many countries. This is due to population growth, change in lifestyle, water pollution, inefficient water use, and climatic changes. Considering the nearly endless water resource in the oceans, seawater desalination is an increasingly attractive solution. Effectively, more than 18 983 desalination plants are in operation in 150 countries worldwide. The capacity was 88.6million m^3/d as of 2016 [1].

Two major desalination technologies types are used for seawater and can be classified as either thermal or membrane processes. The thermal process includes multi-stage flash (MSF), multi-effect distillation (MED), vapor compression distillation (VC) and freezing. When, membrane processes include reverse osmosis (RO), forward osmosis (FO) and electro-dialysis (ED). Moreover, there are other processes, such as ion exchange and hybrid processes (power/thermal distillation/RO). Details and reviews of these all seawater desalination technologies are given elsewhere [2-6]. Nowadays, RO process is the most internationally widespread desalination technology [7]. It represents more than 66% of global capacities of the water produced by desalination [8].

Actually, many technological advances and innovations are trying to improve the industrial seawater desalination processes; essentially, to minimize the process energy consumption, improve the quality of desalinated water and reduce the environmental impact. Despite all this, seawater desalination technologies still imperfect, costly and largely inefficient. Thus, new and sustainable processes development is among the most significant challenges.

In this paper, the freezing separation process is considered for the purposes of seawater desalination. This process presents several advantages [9-11].The objectives of this work are to discuss recent developments and innovations occurring in this freezing separation process and to review and analyze the main methods currently being investigated in this process, especially for seawater desalination. Moreover, the possibility to use hybrid process, actually having significant profits, will be explored in order to propose and develop a new innovative system.

Freezing separation processes

The freezing separation process is based on the fact that, ice crystals formed are made up of essentially pure water when the solution temperature is lowered to its freezing point. It consists of two main processes: ice formation by heat removal and ice washing-separation from the concentrated fluid. Freezing separation process methods and main industrial applications are presented in the following sections.

- ✓ ***Ice formation process***

According to various researchers [12-14], there are two basic freezing separation methods for concentrating solutions: ice suspension and ice film freeze crystallization. In ice suspension crystallization method, ice nuclei are primary formed and then growing in the solution [15-16]. The second method is the ice crystallization as an ice layer on a cooling surface [17-18].

In the industry, suspension freeze concentration is widely known as the Niro method (*figure.1*). It consists of two stages: crystallization and separation of ice crystals. The major components of this process include a scraped surface crystallizer and a wash-separation column. Ice nuclei are formed on the heat exchanger inner surface and then are scraped off by rotating blades. As the ice nuclei growth, solution becomes more and more concentrated. The both obtained concentrated solution and suspended ice crystals are then fed into a wash-separation column. In this system, high purity ice crystals can be attained [19].

The ice film crystallization on a cooling surface consists of the crystals formation that grows layer by layer from the solution to be concentrated. This concentration technology is based on directional freezing, and the most important crystals form is the dendrites [20-22]. While, solute inclusion in ice is difficult to avoid in practical applications [18].

The two methods described for concentrating solutions by freezing separation differ in terms of different aspects. The most important one is the ice growth rate. This later is about 10^7-10^8 (m/s) for suspension crystallization [16-23], against 10^6-10^7 (m/s) for film crystallization [24-25]. Also, ice crystals of high purity can be achieved from continuous suspension crystallization process [19, 10]. Furthermore, the suspension crystallization method is already applied to industrial scale. While many of film crystallization techniques, although only studied at the lab scale, are available for scale-up [26].

- ✓ ***Industrial freezing separation applications***

The most recent freezing separation technology using continuous ice suspension crystallization is widely exploited in many different industrial sectors, especially food and chemical process. Thus, this technology has been developed to a greater extent and several industrial plants are currently available. The success in the food industries was mainly due to its ability to produce high-quality products compared to the available thermal technology. While in the chemical industries, it is generally adopted when there are no other alternatives. Other sectors where major research is currently taking place include the waste streams treatment and investigation into the freezing process for seawater desalination.

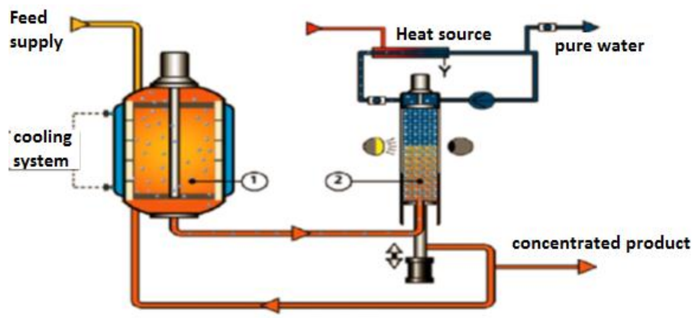


Fig. 1: diagram of the Niro Freeze Concentration Process

As can be found in literature, the food industries have successfully employed the freezing separation technology due to its several advantages [10- 27-30].The main ones are the less energy requirement than other processes, as well as minimal potential corrosion and little scale or precipitation due to the low operating temperatures. The liquid foods concentration using this technique has proven highly efficient. It has been commercially utilized for the fruit and tomato concentration juices [29-30]. Also, it has been employed for concentrating coffee and tea extracts, sugar syrups, maple sugar syrups, dairy products such as milk and whey, and aroma extracts [10].

Furthermore, potential applications of freezing technology also abound in the pharmaceutical, pulp and paper, chemical, and petroleum industries. It is the most applicable when distillation is impossible (azeotropic mixtures, or for isomers with close boiling points) or when distillation becomes extremely energy intensive, for example attaining from 99.9% to 99.99% purity [10]. The method is also applied to the liquid medicine production. Moreover, it is employed to purify organic materials and to concentrate caustic soda, salts, acids, black liquor (from pulp and paper mills), benzene, toluene, xylenes, ethanol and isopropanol.

Another important application of freezing technology is the concentration of waste liquids for disposal. The freezing method was used for slurries or sludge concentration and water purification [14-31]. Also, synthetic waste water and industrial wastewater were purified using the freezing-concentration method and satisfying result was obtained. Moreover, a good purification rates by combining radial freezing and stirring to purify the waste water was attained [10].

Technologically all the freezing separation methods used in the food industries could be used for desalination [10]. The only point to be considered is the economic analysis of the freezing process for desalination since water is a low-value product compared to the foods. However, this one has recently become less important due to the growing attention for more effective solutions to freshwater shortage which is becoming a critical problem in more and more regions worldwide.
In the following section, the main systems which have been studied for the purposes of freeze desalination will be presented.

Freeze desalination developments:

The desalination by freezing allows purified water removal from seawater by freezing crystallization, and separation formed ice crystals from brine. High purity water is then achieved by this process with low energy requirement and important efficiency. Compared to other desalination processes, freezing process offers a numerous advantages [9, 10]. It requires less energy, needs almost no pretreatment and has minimal corrosion and metallurgical problems.
Indeed, the freezing latent heat is lower than the evaporation one (333.5kJ/kg and 2256.7kJ/kg, respectively) [11]. Thus, process energy requirement is potentially reduced. Another freezing process advantage is the absence of chemical pre-treatment; that means no discharge of toxic chemicals into the environment. Moreover, because the freezing process is operated at low temperature, it greatly reduces the problems of scale formation and corrosion, which means less use of chemical reactive and thus a lower operating cost. Also, this permits a wider selection of materials and construction methods that result in lower capital cost. Also, this process is relatively insensitive to substances concentration or type changes in feed water.
Despite all these important advantages of freezing desalination processes, this freezing technique is still in studies form and lab scale units; attempts at its commercial application have not been yet successful until now. This is largely due to a combination of lacking equipment and prejudice ("cooling is always too expensive"). However, these caveats have become recently less important. This has resulted firstly of the freezing separation technologies development to a greater extent in several industries and secondly of the growing attention to exploring more effective solutions to potable water shortage that is being actually a very critical problem in more and more regions worldwide. Moreover, many papers have been studied different freezing desalination systems. Most of them concern the simulation and theoretical analysis of freezing processes. Experimental studies on these systems are still very limited.
Mahdavi et al. [32], have studied the non-direct contact external cooling crystallization method for seawater desalination. Tests with samples from the Boshehr beach showed that drinking water can be produced after three freezing desalination cycles.

Mandri et al [33, 34] have tested a pilot crystallizer consisting of a cooled tube immersed in a cylindrical double jacketed tank (*figure 2*). The desalination feasibility by indirect freezing in one stage process operation was investigated. The whole process involves a freezing step, leading to the ice layer crystallization and a sweating step. Authors have been showed that the impurities contained in the ice layer formed during the crystallization step are in the form of brine pockets trapped inside of the layer; and thus the sweating step has been shown to efficiently complete the purification by draining out of the trapped solution pockets inside the ice layer.

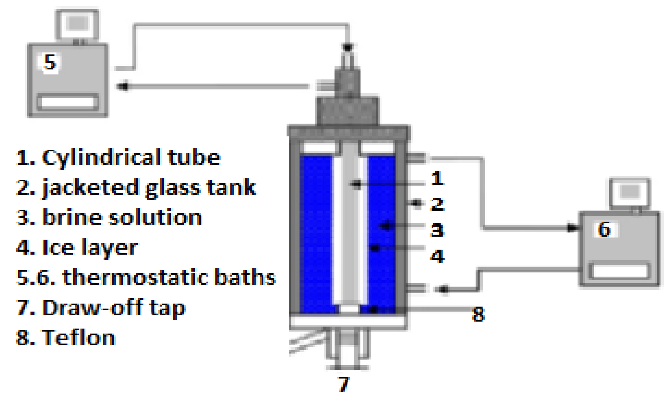


Fig. 2: Schematic view of experimental setup [34]

Also, the progressive freeze concentration technique (PFC) has recently been applied to desalination [35] (*figure 3*). The experimental results showed that the technique is useful not only in food processing but also in desalination. The progressive freeze concentration improvement has been done particularly in its apparatus design to obtain a better product quality. Several new designs for PFC system have been introduced, constructed and operated under different conditions; especially on solution movement such as stirring [36, 37], ultrasonic radiation [38, 39], bubble-flow [40], agitation and aeration and also by oscillatory motion. It has been showed that there are several factors affecting the system efficiency and the thawed ice quality [41] including circulation flow rate, initial concentration, coolant temperature, and circulation time. According to Hanim et al [42] further studies on different process parameters are necessary for enhancing the PFC system performance.
Another system which has been studied for the purposes of freeze desalination is heat pump systems. A new system (*figure 4*) utilizing the heat flow of a heat pump to increase the whole system efficiency was proposed [43]. In the suggested system, the ice washing and melting process occur at the same place by reversing refrigerant flow through the vapor compression cycle. So there is no need for an ice handling mechanical systems. Rane et al have also proposed a heat pump system [44] which selectively freezes water from seawater in the evaporator and melts the ice in the subsequent phase when it serves as a

condenser. The suggested heat pump systems were proven as an energy saving processes.

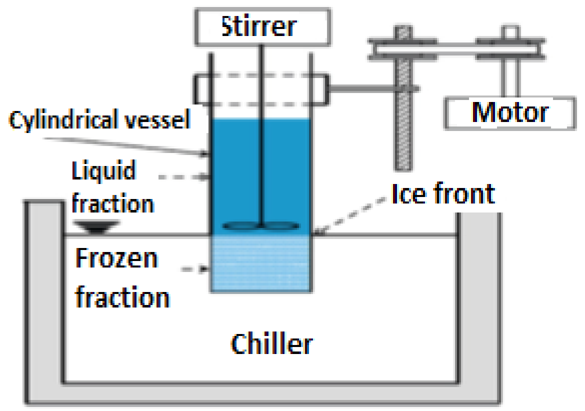


Fig. 3: Progressive freeze desalination unit [35]

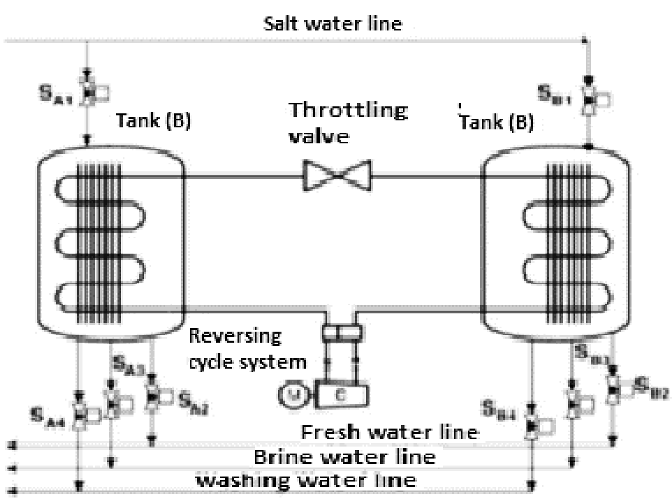


Fig. 4: Layout of freeze water desalination system using reversed vapor compression heat pump [43].

New freezing methods for seawater desalination have also recently been proposed. One of these methods is that water has been frozen by passing dry air in a 0°C environment over seawater [45]; a theoretical model of this desalination process was built and was verified through experimental testing. The second process, HybridICE™ technique, consists of a refrigeration unit and scraped surface heat exchangers [46] (*figure 5*). Authors have used three methods (titrimetric, conductometric, and colorimetric methods) for analyzing the ice produced purity. The HybridICE technique was found to be a viable desalination technology for producing high-quality water (but not pure fresh water), at low energy consumption, and it can be easily combined into existing refrigeration systems.

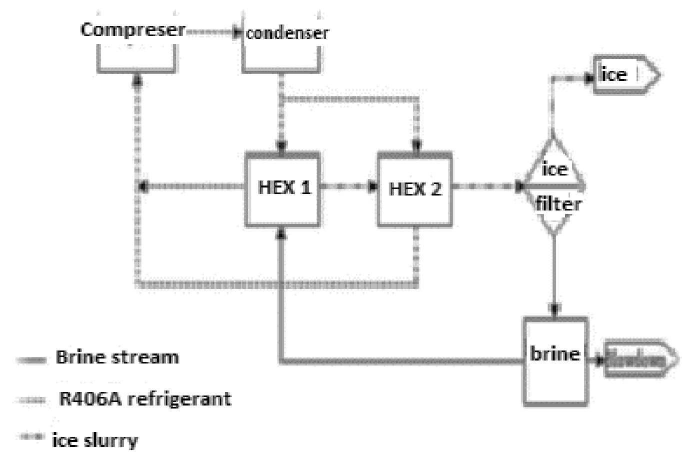
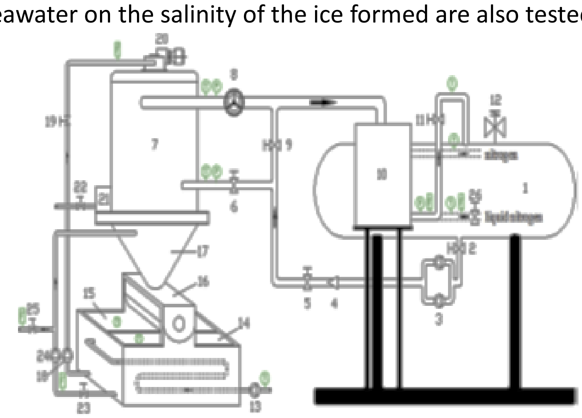


Fig. 5: HybridICE pilot plant process flow block diagram [46]

Badawy [47] has studied freezing desalination of seawater from Umluj Beach in Saudi Arabia by laboratory experiments using non-direct freezing. The results showed that the salinity of ice could be reduced to a very low level by several continuous cycles of the freezing-melting process.

Lin et al. [48] also proposed and designed a prototype for desalination of seawater by freezing (Figure 4.6). In this system, R410A is chosen as a secondary refrigerant to transfer cold energy from liquefied natural gas (LNG) to seawater, and a suspended ice machine is used to produce ice. Experiments are conducted with the prototype. The results show that the salt removal rate of the system is about 50%, indicating that a single desalination cycle is not sufficient to produce potable water. More desalination cycles, or reverse osmosis assisted desalination desalination, are required to produce drinking water. The influences of certain key factors, such as the evaporation temperature of the refrigerant, the flow of seawater on the salinity of the ice formed are also tested.



1-R410A cycling barrel,2,5,6,8,9,11,19,22,2323,25,26- valve,3- electromagnetic shielding pump,4-check valve,7- ice making backet (flake ice maker), 10-heat exchanger,12- safety valve, 13,18,24- water pump,14- ice melting tank,15-mixing tank,16-separator, 17-ice-washing chamber,20-water distributing tank,21-concentrated seawater collector

Fig. 6: prototype de dessalement par congélation et GNL [48]

As a conclusion, despite the tremendous researchers that have currently investigated a variety of freezing separation techniques for desalination, its use is still limited due to the limited know of the optimum technique for freezing and separation ice. It is almost impossible to obtain pure ice crystals by freezing method alone. Ice quality is influenced by some factors during the freezing process. Highly saline water trapped in the ice that means that seawater ice obtained, although purer than seawater, is not pure fresh water [49].

In the following section, a possible use of a hybrid system where freeze desalination is combined with other desalination technique will be discussed.

Hybrid desalination process (freeze separation – other desalination technique)

Numerous previous published articles of freeze desalination studies have mentioned that there is a high potential of combining the freezing process with other desalination techniques. This hybrid approach could provide a synergy to the desalination process. One of the most promising ones is the combination of reverse osmosis and freezing process.

✓ ***Hybrid desalination process studies review***

Most of hybrid desalination process studies [9, 50, 51]; discussed the possible use of a hybrid system where freeze desalination is used to process and re-use of the concentrated brine for an RO system. These processes are proposed as an efficient system to reduce the environmental impact of concentrated reject brine from seawater desalination plants. Furthermore, these hybrid technologies have the potential to increase total plant yield and introduce the prospect of reducing both the use of natural water supplies and waste from these systems.

Another hybrid desalination process, comprised of indirect-contact freeze desalination by ice layer formation and direct-contact membrane distillation in an attempt to utilize the waste cold energy released from re-gasification of LNG, was studied [52]. By optimizing the freeze desalination operation parameters, high-quality drinkable water with a low salinity was produced. At the same time, the membrane distillation process produced ultrapure water. The overall process was proven as an energy-saving process and utilization of LNG cold energy could greatly reduce the total energy consumption.

Kim et al. [53] were proposed a hybrid forward osmosis (FO)/ crystallization/ reverse osmosis (RO) process for seawater desalination. The process theoretical analysis was conducted. The FO unit is considered as the main desalination unit, the crystallization and RO units are regarded as a draw solute recovery process. As a result, the feed stream of the RO process has lower concentration, and consequently, total energy consumption is expected to be reduced. Through the hybridization of these three-unit processes, the energy requirement for fresh water production can be reduced. Thus, it is concluded that the proposed process can be highly competitive.

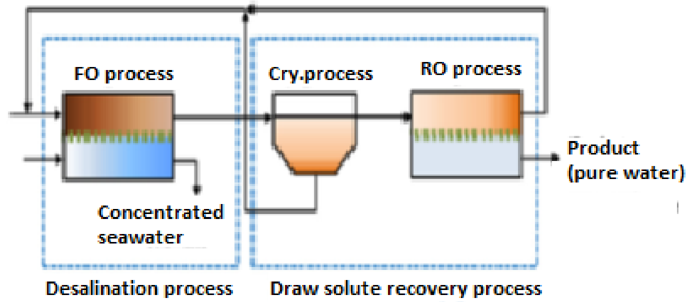


Fig. 7: Schematic illustrating the concept of the proposed hybrid process [53]

✓ ***Proposed hybrid seawater desalination***

In view of main results obtained in this review, considering the advantages of the freezing separation method and the main constraint that is almost impossible to obtain pure ice crystals by freezing method alone, we supposed that the method can be used for seawater pretreatment for reverse osmosis desalination system.

In fact, conventional pretreatment methods, which have been widely applied in seawater reverse osmosis (RO) plants, are not effective in preventing RO membrane fouling and incapable of producing a consistent feed to the RO system. The approach to pretreatment in RO desalination plants has undergone gradual changes and improvements, from the conventional chemical/physical pretreatment process to membrane-based pretreatment and finally integrated/hybrid membrane systems. However, future efforts should be undertaken to ensure RO desalination industry competitively and successful.

Since the pretreatment system effectiveness is usually accessed through its performance, which includes the permeate quality, membrane lifespan, membrane fouling tendency and cost; the freezing separation process as pretreatment in RO fulfilled these criteria. It presents several advantages such as insensitivity to changes in the concentration or quality of feed seawater. Also, it offers relatively pure fed solution into the RO module compared to conventional and membranes pretreatment processes. This means fewer foulants, lower operating pressure in RO module and higher membrane lifespan. Therefore, costs of the pump and membrane can be reduced, and high-quality of produced water can be obtained.

The proposed hybrid process involves three main steps: filtration for removing the suspended solids of feed seawater, pre-treatment by freezing process and RO modules desalination. Figure7 represents the basic diagram of the hybrid process proposed.

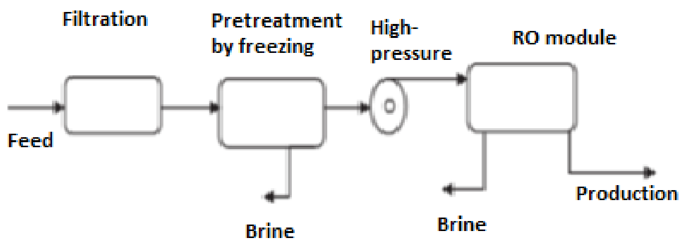


Fig. 8: Basic diagram of the proposed hybrid seawater desalination.

In order to recover the process energy, the freezing unit is coupled with a heat pump system, and the feed seawater is pre-cooled by heat exchange with brine rejected and water pre-treated. The pre-cooled seawater is then pumped into the crystallizer scraped surface heat exchanger (SSHE) where ice crystallization is conducted. Pure ice particles crystallized are scraped and entrained by concentrated seawater flow. The suspension obtained is sent to a separation column. Then, obtained ice crystals are melted in the melting chamber. The pretreated seawater by freezing is then sent to reverse osmosis module to be desalted.

As future work, the proposed hybrid process feasibility will be studied. This work will be based on an experimental study with the proposed freezing process test stand, and also, a study of seawater freezing pretreatment effect on the RO feed water quality in order to optimize the hybrid process and the energy required.

Conclusions

In this paper, the freezing separation process applications in different industries have been explored. Three applications seem to be winning favors of freezing separation process are: concentrating fruit juices, purifying organic chemicals, and treating hazardous wastes. The main reasons for these successes are due to the development of more efficient and high capacity process, and high purity or quality products. In the other hand, although different researchers have currently investigated a variety of freezing separation technologies for seawater desalination, the optimum technique for freezing and separation ice is neither enough known nor well controlled.

From the recent work which has been assessed in this paper, it has been shown that freezing separation technology seems to be very successful when employing a hybrid process that combines freezing process and other seawater desalination technologies. Thus, we have proposed a new innovative solution to potable water shortage. A hybrid process that is consisting in combining freezing technology upstream reverse osmosis (RO) module for seawater desalination was suggested.

The proposed hybrid process seems to have the potential to reduce energy consumption and increase produced water quality. It presents several advantages such as insensitivity to changes in the feed seawater concentration or quality. Also, the freezing pretreatment offers relatively pure fed solution into the RO module compared to conventional and membranes pretreatment processes. This means fewer foulants, lower operating pressure in RO module and higher membrane lifespan. Therefore, costs of the pump and membrane can be reduced.

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