DESALINATION: MAKING SEAWATER POTABLE

Abstract

Desalination is one of the oldest known processes where salty seawater is converted into drinkable fresh water[1]. In nature, this occurs when seawater gets evaporated and collected in a cloud, ultimately falling on the ground in the form of rainwater, thus replenishing the groundwater level. The desalination technique has gained huge importance in recent times to meet the never-ending need for fresh water. This process of purifying water and making it potableholds immense potential. But to prepare the seawater for desalination, we must remove large debris and organic matter from it. This phase is known as the pre-treatment phase. Desalination, the treatment phase, includes various techniques. These vary from utilizing thermal energy, membrane distillation, ion-exchange technology as well as new upcoming technologies such as gas hydrate or freeze crystallization in order to make seawater free from salts. After desalinating seawater, the water is then disinfected, re-mineralized and made potable for drinking. This book chapter contains all the three phases of water treatment thereby helping us to understand that how the seawater is made fit for home.

Keywords : Coagulation, Flocculation, Nucleation, Antiscalant, Dissolved air floatation, Multi-stage flash, distillation, Multi-effect distillation, Mechanical vapor compression, Nanofiltration, Gas hydrates, Freeze crystallization, Eutectic point, Fluoridation

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I. INTRODUCTION

Desalination has been known for a long time and has been considered one of the major sources of freshwater production from seawater. Aristotle, the Greek philosopher referred to this process in his work – "Meteorology". He mentioned that salt water can be turned into sweet water by turning it into vapor. He also discussed how a water-holding wax vessel which when submerged in seawater, can filter out the salt leaving behind the sweet water. It has also been reported that to meet the freshwater requirement, the sea sailors boil the seawater in a vessel and utilize the sponge to close the mouth of the vessel[2]. The water vapor when evaporated gets trapped in the sponge. Therefore, the freshwater was collected by squeezing the sponge. About 2000 years ago in China, people observed that the bamboo mats that were used for cooking rice formed a layer that had salt adsorption and ion exchange properties. In modern times, associations like the International Desalination Association (*https://idadesal.org/*) are serving as a platform where many scientists, engineers, researchers from various fields, and consultants unite to find new solutions and techniques to desalinate sea or brackish water so that the world can meet the rapidly growing demand for clean and drinkable water. Currently, the whole world knows the importance and immense potential of desalination. Seawater is a huge reservoir of water and turning this into potable fresh water is the hope of future generations.

Countries like Kuwait, which doesn't have any permanent source of fresh water in the form of rivers, are heavily dependent on the desalination of seawater. Currently, there are more than 6 desalination plants in the country.

II. BEFORE DESALINATION: THE PRE-TREATMENT

Before starting the process of desalination, there is a requirement to prepare the incoming source of water for the treatment (Figure 1). The following operations are performed in the pre-treatment phase:

1. **Withdrawal of Water from Source:** For desalination, the seawater or the brackish water is withdrawn through giant pipes by employing powerful pumps.

2. **Screening of Water:** This step involves the removal of large debris, including algae, sticks, logs, plankton, etc. from the water, that will otherwise interfere in the purification step[3].

3. **Regulating the pH of the Water:** the pH of the seawater may vary from 7.5 to 8.4. Therefore, this alkaline pH may have varying effects on the subsequent treatment of water. Regulating the pH of water is important for minimizing the mineral depositions and corrosion of infrastructure as well as, and this will also protect the filtration membranes from fouling. Also, it is important to note that the chemicals involved in downstream water treatment may be pH-dependent. Therefore, adjusting the pH of water is an important criterion.

4. **Coagulation and Flocculation:** Augmentation of certain chemicals will help in facilitating the removal of colloidal and suspended impurities from water so that the water can be easily filtered and utilized for downstream treatment. First, we add certain

coagulants like ferric chloride or alum to neutralize the negative charge of some particles thereby leading to the formation of some stable aggregates i.e. nucleation of aggregates. This step is known as coagulation. Then we further add flocculant which are chemicals that in turn promotes the growth of the coagulated particles or by natural Brownian motion the coagulated matter adhere and grows, thereby leading to the formation of massive flocs. Thus coagulation and flocculation processes are complementary to each other and both are necessary for water treatment[4].

5. **Sedimentation, Antiscalant Injection followed by Filtration:** The water which has undergone coagulation and flocculation processes, is then exposed to sedimentation. During the sedimentation process, the flocculated and coagulated mass is allowed to settle down pertaining to its large weight and massive size in big tanks or basins. Water free from sediments is then collected from the top of the tanks. After the removal of the sediments, another problem that needs to be addressed is the presence of calcium and magnesium ions as well as other heavy minerals in seawater that can lead to the scale deposition and damage of downstream filtration membranes and other equipment[5]. Therefore, water is first analysed for the presence of such mineral ions and accordingly appropriate amount of antiscalant chemicals are injected into the water. These chemicals work by three means-

   - by increasing the solubility of minerals in water, thereby preventing their precipitation.
   - by disrupting the formation of nano-crystals of heavy minerals in water, thereby, this will hinder the formation of large deposits.
   - by playing the role of dispersant thereby preventing minerals from aggregating together.

   After antiscalant injection, the water is then passed through a bedding of membrane filters that helps in the removal of any chunks or suspended particles present in water.

6. **Dissolved Air Floatation (DAF):** This treatment is required to remove impurities like oil or turbidity caused by algal bloom[6]. The basis of this technique is the utilization of air bubbles in floating up the suspending pollutants in water to the surface for their removal. Thus, after undergoing this process water becomes free of oily, or greasy material[7].

7. **Activated Carbon Adsorption and Chemical Treatment of Water:** Water flows from bedding that is coated with Activated carbon such as anthracite coal (86-97% carbon-containing). This helps in removing odor and organic compounds from water[8]. Also, disinfectants such as chlorine are added to prevent the growth of any harmful microorganisms.

8. **Water Storage:** After performing the mentioned pre-treatments of water, it can be stored in large tanks for days or months until there is a water desalination requirement. During this time, if there is any impurity in water, it can settle down, thereby further purified water can be collected from the top of the storage tank.

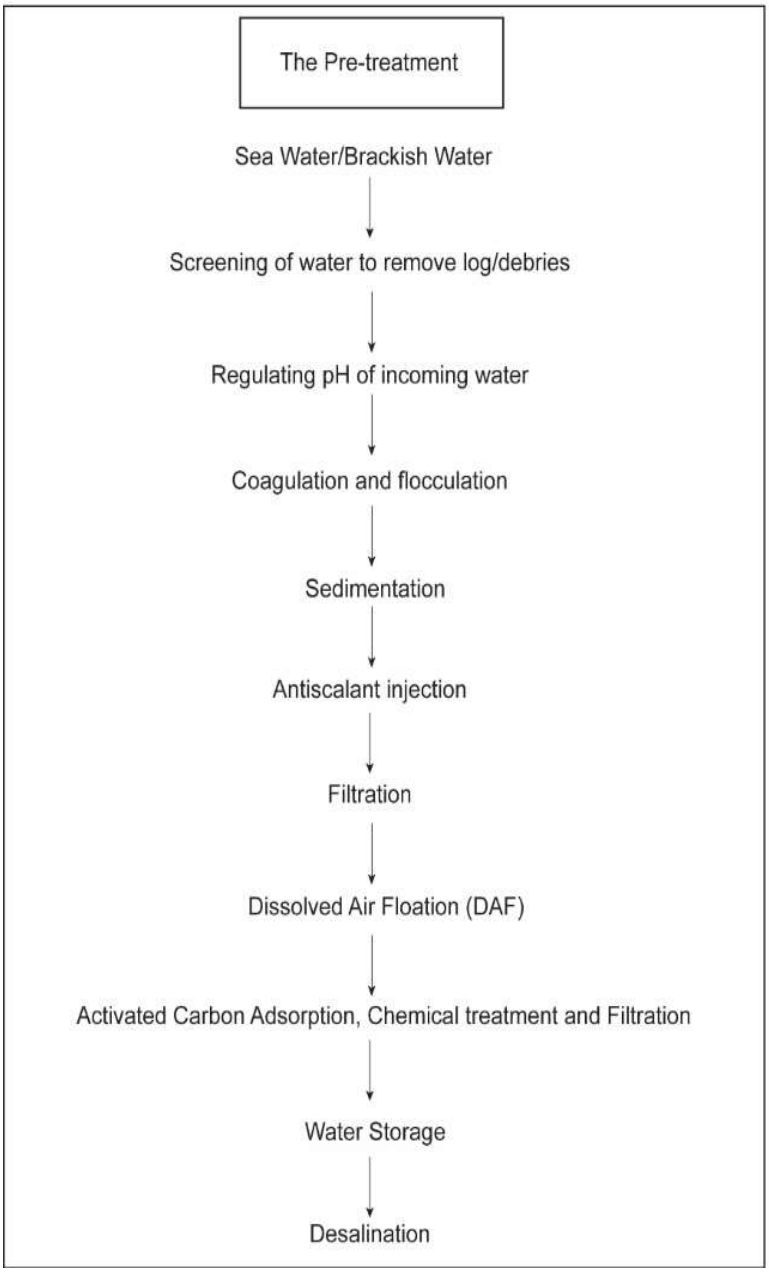

Figure1: Schematic outline of the pre-treatment process.

III. DESALINATION: THE TREATMENT

The desalination technology (Figure 2) can be classified into 4 broad categories-

1. Thermal desalination
2. Membrane desalination
3. Ion exchange desalination
4. Gas hydrate and freeze crystallization

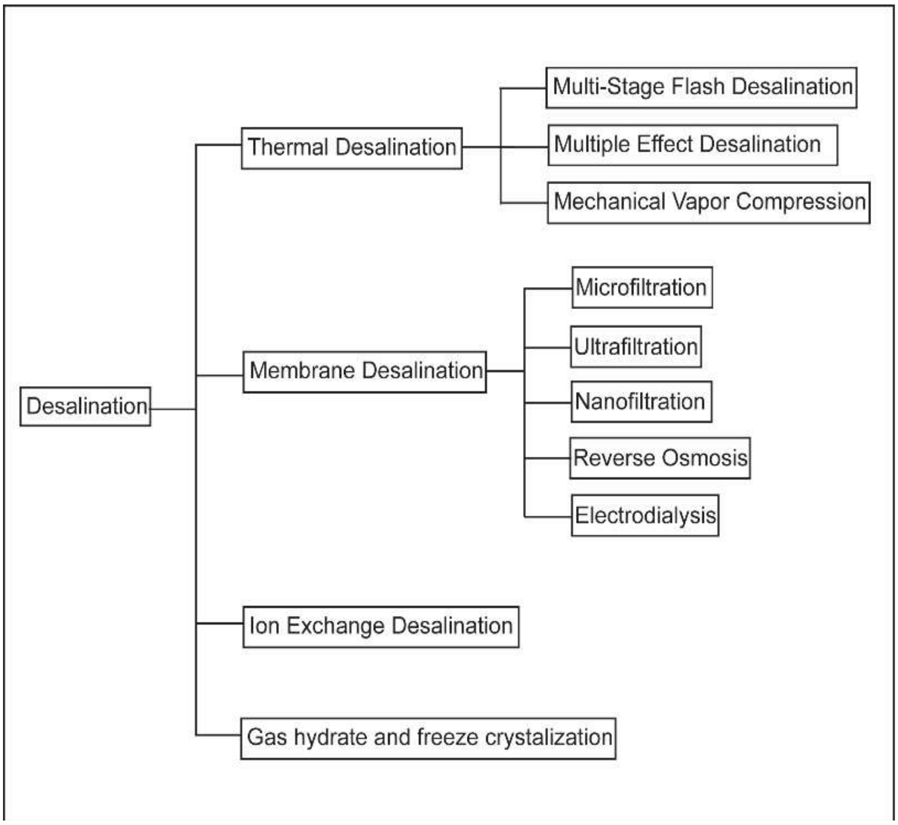

Figure 2: The different techniques involved in desalination of seawater.

1. **Thermal Desalination:** Thermal desalination is based on the traditional distillation technology where water is boiled to produce vapor and then potable water is recovered by condensation of vapor. However, with time there have been several modifications in this distillation process.

    - **Multi-stage Flash Distillation (MSF):** To understand the process of MSF, let's first understand the principle of MSF. Flash distillation is a process where the fluid is heated as well as pressurized and then passed through a valve into a region of lower pressure. This sudden change in pressure causes some amount of liquid to be vaporized as a flash (as the state conversion is so fast) while the remaining liquid is collected and then again fed to the system to produce more vapor.

      Employing this principle, MSF incorporates multiple stages of flash distillation to purify fresh water from seawater[9]. Here, with each successive stage, there is a pressure drop which leads to the conversion of saline water into water vapor. At last, the freshwater is collected while leaving behind the concentrated brine solution as a by-product (Figure 3). MSF involves the following procedure-

      - The seawater is first preheated before entering into the MSF plant.
      - The water then enters into one stage where flash distillation occurs pertaining to the drop of pressure and then it goes to the other stage which is interconnected, where there is more drop in pressure, thereby leading to more vapor production and the event goes on.

- The vaporized water molecules get collected at the top of the stage.
- Vapor from the previous stage is passed from a condenser so that water condensation happens (while the heat transferred upon water condensation can be utilized to preheat another source of incoming saline water, a technology utilized in multi-effect distillation).
- Once the water vapor condenses into fresh water, it is fed to the second stage where the flash distillation process is repeated. This cycle of flash distillation and condensation then again feeding to the next stage, is repeated several times to remove salts from seawater and make it drinkable.
- After many cycles of flash distillation, the freshwater which is devoid of any salts, is collected for future use while the concentrated brine left behind is discharged into seawater with further considerations.

MSF distillation is a scalable and reliable technology that utilizes less energy consumption than normal distillation. However, due to the need to pre-heat the seawater, the MSF technology is not fully independent of the energy source. Also, the concentrated brine produced at last should be very carefully managed as releasing it directly into seawater can cause huge damage to aquatic flora and fauna. The huge concentration of salts in liquid brine can lead to scaling and corrosion of infrastructure.

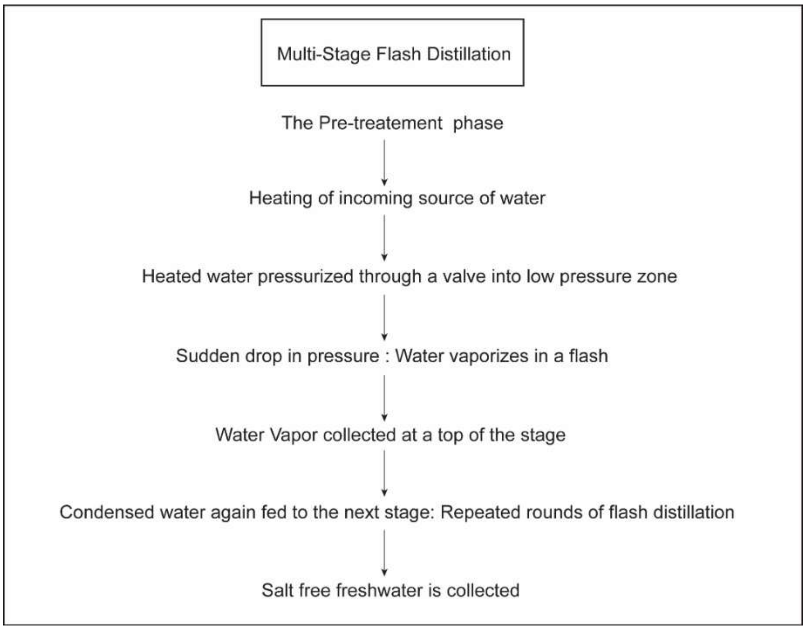

Figure 3: Flow chart representing the multi-stage flash distillation procedure.

- **Multi-effect Distillation (MED):** MED works on the same principle as that of MSF, but it also utilizes the heat released during condensation of water vapor into liquid state, to heat the subsequent water influx. Therefore, MED is more energy efficient than MSF.

- **Mechanical Vapor Compression (MVC):** This method employs mechanical compression of water vapor to increase the saturation temperature of water vapor, thereby facilitating the condensation of vapor into liquid fresh water[10].

MVC involves the following processes-

- **Production of water vapor-** the incoming seawater is heated to produce water vapor. This vapor already contains heat as a form of energy, due to its state conversion.
- **Mechanical compression of water vapor**- water vapor produced is further compressed. This increases pressure leading to a rise in the temperature of water vapor above its saturation.
- **Condensation of water vapor**- the compression of water vapor causes a temperature rise. Therefore, as soon as the temperature is decreased or the system is cooled, the water vapor then changes its state back to liquid. To make this process more energy efficient, the heat released during the condensation step is retrieved to heat the incoming saline water.
- Utilizing the MVC process, the freshwater is collected for later usage, while the liquid brine that contains huge amounts of salts is discharged back into the seawater.

This technique is energy efficient and suitable as even low levels of waste heat can be engaged. As well as, this technique is adaptable at a variety of scales, ranging from small to huge desalination plants. However, this technique requires compressors, thereby increasing the installation as well as the overall maintenance of the desalination plant.

2. **Membrane Filtration Processes in Desalination:** Membrane filtration procedures involve the separation of solutes and salts from water by selective semi-permeable membranes. The energy used here can be pressure or electric potential. The membranes provide passage for water molecules while inhibiting the passage of ions and other particles.

Broadly membrane desalination can be classified into the following groups –

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis
- Electrodialysis

- **Microfiltration** depends upon size exclusion and provides passage to water and smaller particles whereas retains larger size particles.

- **Ultrafiltration** also depends upon size exclusion but the pore size is smaller than microfiltration which retains even smaller particles and macromolecules[11]. Further

- **Nanofiltration** uses both size exclusion and charge to allow water molecules while blocking the passage of ions and salt molecules[12].

- **Reverse osmosis** is a widely accepted and highly used desalination method in the present scenario due to its reproducibility and effectiveness. In reverse osmosis, seawater or saline water is pressurized and forcibly passed through a semipermeable membrane. The pores of the membrane allow the passage of water while blocking the ions and other solutes. In this way, it produces a concentrated brine over time and it builds osmotic pressure to revert the process. However, the applied high pressure counteracts the osmotic pressure to maintain a steady production of freshwater. The freshwater (also known as permeate) is collected in a chamber while the brine is disposed of back to the sea following proper disposal protocols and minimizing environmental impacts[11].

- **Electrodialysis** utilizes ion-selective membranes and an electric field. It includes alternating cation- and anion-exchange membranes. In the presence of an electric potential the cation migrates towards the cathode and anion migrates towards the anode through cation exchange and anion exchange membranes respectively. Electrodialysis can be categorized into either continuous flow ED or batch mode ED. In continuous flow, the water flows continuously through stacks and ion exchange membranes are separated by spacers. Whereas in batch mode, water is desalinated in different compartments in different batches using the ion exchange membranes[13].

❖ **Advancements in Membrane Desalination**

- **Graphene Desalination:** The rapid development of nano-assisted reverse osmosis membrane allows to desalinate the saline water more precisely and cost-effectively. The graphene sheet was modified in such a way that multiple nano-size pores are introduced in it so that only water molecules can pass through while the salts and other macromolecules can be retained. The charge and hydrophobic nature of the membrane, helps in removal of undesired solvent molecules. Along with that graphene has high mechanical strength and can purify water in a very marginal thickness. That means at low pressure graphene desalination is possible which will save more energy[14].

- **Molybdenum Disulfide (MoS_2) Nanofiltration:** MoS_2 is a two-dimensional material having very thin layers (in the nanometer range) which helps in fast water transport across the membrane. Along with that, it can be engineered to have selective ion permeability enabling it to be better at salt rejection. Though MoS_2 membranes show promising results on a laboratory scale, large-scale membrane production is challenging as well as achieving high salt rejection with minimized fouling on a large scale is difficult. However, the tunability, durability, and potential to be integrated with existing systems such as RO makes it a potential application for desalination in the future[15].

3. **Ion-exchange Desalination Technique:** This desalination involves a matrix or ion exchange resin that removes undesired ions from the incoming source of water. The resin is composed of functional groups that carry opposite charges to remove the undesired ions[16]. There are mostly two types of ion exchange columns- anion exchange and cation exchange.

- **Anion Exchange Column:** This resin targets anions (negatively charged ions present in water). It helps in the removal of sulphates, chloride, and nitrate ions while replacing these with another ion, like hydroxide, from the resin.

- **Cation-Exchange Column:** This resin targets cations i.e. positively charged ions for their removal from water which may include the removal of calcium and magnesium ions and replacing them with sodium or hydrogen ions.

  The ion exchange plants help in the removal of specific types of ions from water. Therefore, it is very beneficial in the treatment of wastewater produced by industries. Also, this type of desalination helps to remove the hardness of water.

  However, with repeated use of the resins, there comes a time when they become saturated. Therefore, we must regenerate the resin. Also, this technique requires special types of resins for the removal of specific species of ions. Hence, it is more expensive and requires maintenance from time to time.

4. Gas Hydrate and Freeze Crystallization Technology

- **Gas hydrates or clathrates** are ice-like compounds having gas molecules entrapped in lattice structures of water molecules[17]. It is naturally formed at low temperatures and high pressure generally in the deep ocean or polar regions. The gas molecule that is generally entrapped is methane but it can be CO_2, ethane, propane, or hydrofluorocarbons.

  Gas hydrates are composed of 85% of water hence they can serve as a source of pure water. Gas hydrate-based technologies are widely accepted and studied worldwide to produce pure drinking water from saline seawater.

  To form a hydrate it requires lower temperature, high pressure, a hydrate former (gas molecule such as methane, propane), and water. Combining the guest gas molecule with saline seawater under suitable conditions for hydrate formation leads to the formation of hydrates and hydrate cages. This way the salts cannot enter into the hydrate structure but rather remain in the surrounding aqueous phase. Following thermal heating or putting pressure, the hydrates can be dissociated into gas and freshwater.

  The gas hydration method involves hydrate nucleation, growth, and dissociation. When optimum conditions such as low temperature and high pressure are obtained inside a reactor in the presence of a hydrate former, nucleation begins. The switch between unstable conditions to stable structure formation is called nucleation. The stability of hydrate formation depends on temperature, pressure, gas compositions, and thermodynamic behavior of the gas system. Whereas nucleation depends on the energy barrier, driving force towards hydrate formation, the critical size of nuclei, and the rate of nucleation.

- **Advantages:**
  - Energy efficient method compared to thermal plants or reverse osmosis process for freshwater production from saline water.
  - Gas hydrates can be formed using the same hydrate former making the process cyclic and sustainable.

- It does not require high pressure as used in reverse osmosis making the design simple and reducing the chances of damage to the reactors.
- This process generates a very concentrated brine solution due to the selective capture of the water molecule. So the volume of waste generated in the form of brine is less in gas hydrate technology compared to traditional gas hydrate technologies.
- If greenhouse gases are used as hydrate formers,it will be beneficial for the environment, as excess amount of the free greenhouse gases negatively affect the environment.

- **Limitations:**
  - The key limitation of gas hydrate technology is that the hydrate crystals can not be easily separable from the concentrated brine solution.
  - The usage of hydrofluorocarbons such as SF_6, CFC, HFC, and HCFC as hydrate formers will lead to environmental damage such as ozone depletion.
  - Alkanes and cycloalkanes hydrate formers are flammable.
  - Reactors are not designed for full recovery of the hydrate gas former thus increasing the cost.

IV. FREEZE DESALINATION

The freeze-concentrationbased desalination or freeze desalination (FD) process produces ice crystals in saltwater thereby generating freshwater ice crystals and concentrated brine[18]. Freshwater is obtained from the ice crystals by melting them. Ice crystals have small dimensions thus they do not include salts or other impurities during crystallization. Therefore, the freeze desalination process increases the concentration of the aqueous phase as the salts remain in the aqueous solution. So, the separated solute needs to be mixed with liquid otherwise they will be entrapped in between the growing ice crystals. This procedure is energy effective as it requires only 1/7th energy required for vaporization-based desalination processes.

FD can be classified into – direct contact methods and indirect contact methods[18].
The direct contact method involves a volatile refrigerant that is directly mixed with saltwater. When the refrigerant vaporizes it takes the heat away from the saltwater and induces the formation of ice crystals. As more of the refrigerant vaporizes the size of the ice crystals also increases and remain suspended in the concentrated saltwater (Figure 4, A). The refrigerant is collected and can be reused.

The indirect contact method involves a wall between the saltwater and the refrigerant. The refrigerant is poured on the outer side of the wall and inside it induces the formation of ice crystals (Figure 4, B). The indirect contact process is further categorized into suspension freeze concentration (SFC) and layer freeze concentration (LFC).The SFC process involves the following steps – nucleation, crystal growth, and crystal separation. In SFC ice crystals remain floated on top of a concentrated salt solution and need thorough post-desalination cleaning to remove any salts on the crystal surface. Whereas in LFC ice crystals formed on the wall in a single layer leaving concentrated salt solution on the top of the ice layer.

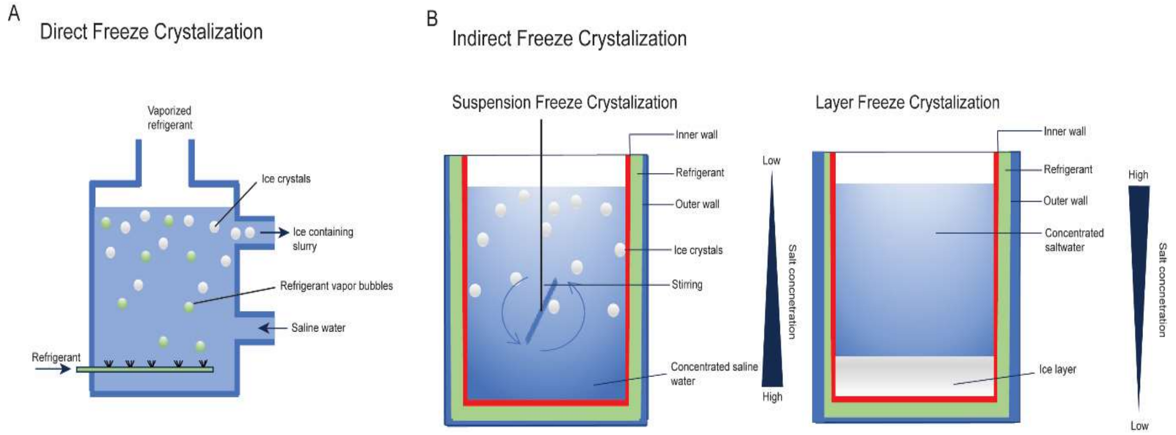

Figure 4: Diagrammatic representation of different types of freeze desalination. Panel A represents direct freeze crystallization, while panel B represents indirect freeze crystallization.

The formation of ice crystals and ice-salt hybrid crystals in freeze crystallization depends on salt concentration and the temperature of liquidus saltwater. When freezing desalination of saltwater begins the salt concentration gradually increases and this leads to a decrease in the liquidus temperature. The phase diagram of NaCl-H_2O solution depicts that there is a eutectic point which indicates at a certain salt water concentration and a certain temperature NaCl (i.e., salt) starts crystallization along with ice crystals (Figure 5). The eutectic point is the lowest limit freezing point of the mixture and the highest limit of salt dissolved in saltwater. The process of simultaneous ice and salt crystal formation is known as eutectic freeze crystallization. The ice crystals float in the saltwater whereas the salt crystals settle down at the bottom making easy separation of the ice crystals from the concentrated saltwater.

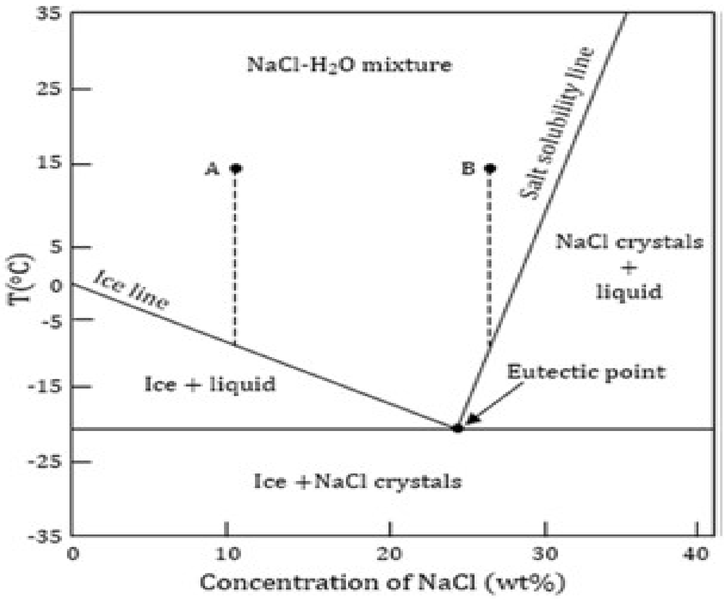

Figure 5: Equilibrium phase diagram of NaCl-H_2O solution. Depending upon the initial salinity, solidificationof the salt solution follows either the ice line or salt solubility line. (Source- Najim Abdul. NPJ Clean Water. 2022; 5:50)

1. **Limitations:**
   - The ice crystals often get contaminated by the concentrated saltwater thus it requires extensive post-desalination operations.
   - The pre-desalination operations, ice-crystal formation, and post-desalination operations are not done in a single unit which makes the job laborious and cost-ineffective.
   - The procedure is slow compared to other desalination methods.

2. **Advantages:**
   - Energy efficient process compared to other desalination methods.
   - Less fouling and corrosion of the equipment involved in freeze desalination.
   - The latent heat released during the freezing process can be recovered and used in other systems of the facility.
   - Liquified natural gas (LNG) can be used as the energy requirement of the freeze desalination process. LNG can also be used for the generation of electrical energy which can power the freeze desalination plant and other desalination methods in a hybrid mode.

V. DESALINATION: THE POST-TREATMENTS

After the initial desalination procedure, the freshwater was further processed to meet the quality and standards of drinking water (Figure 6). In general, the procedures include the following–

1. **Disinfection:** Post-treatment disinfection is accomplished with the usage of chlorine, chloramine, and exposure to UV light[19]. This kills the microorganisms and pathogens that survive the desalination process. Further, these processes can be coupled with activating photolytic materials such as titanium dioxide, and palladium which can potentially inactivate viruses.

2. **pH Adjustment:** Desalinated water usually has a low pH due to the removal of alkaline ions during desalination processes. The alkalinity of the water depends on the presence of bicarbonate, carbonate, and hydroxide ions. Increasing the alkalinity leads to a lower corrosion rate of the supply pipelines and results in fewer changes in the pH of distributed water due to the release of H^+ and OH^- ions. However excess alkalinity may cause scaling and deposition of salts on the distributing pipelines. Therefore, the pH of the water must be adjusted.

3. **Dissolved Oxygen:** Due to various desalination processes amount of dissolved oxygen varies in desalinated water. It is crucial to maintain an appropriate level of oxygen for standard water quality and aquatic life. After desalination, through aeration (flow of air/oxygen to the water and agitating the surface of the water to dissolve) or oxygen injection or biofiltration, oxygen is added to the water. The level of oxygen was monitored using Dissolved Oxygen (DO) measurements. Dissolved oxygen if present in excess leads to corrosion of iron and also hinders the buffering capacity of various ions. Therefore, an appropriate amount of DO should be maintained to make the water potable and ready for future usage.

4. **Remineralization:** Remineralization is the process of adding the minerals that were lost during desalination processes and are normally present in the drinking water. In this process, mineral salts like calcium chloride, magnesium sulfate, and sodium bicarbonate are added in a regulated manner to meet the water quality with desired mineral levels. Recent advancements include installments of calcite contractors which are remineralization filters that dissolve minerals in the form of limestone media and maintain the alkalinity of the water. Fluoride ions are added through a process known as fluoridation[20]. The remineralization process is monitored by measuring the pH, alkalinity, and concentration of a mineral/salt.

5. **Carbon Filtration:** To remove the residual trace organic contamination and disinfection by-products from treated water, activated carbon filters are used. It will help to enhance the taste of water and remove potential health hazards.

6. **Chlorination or Dechlorination:** Chlorine is often used as a disinfectant to remove the residual microorganism load. Further dechlorination is done to remove excess chlorine before distribution to consumers.

7. **Monitoring and Quality Control:** Parameters such as pH, residual chlorine, presence of organic matter, turbidity, DO and specific ions are regularly monitored in the potable water during the post-desalination processes to match the quality of natural water.

8. **Distribution and Storage:** The desalinated water after multiple treatments and quality checks finally distributed to the consumers through pipelines or stored in chambers. The pipes and chambers are regularly checked for contaminations and proper maintenance of the system ensures water quality throughout the delivery process.

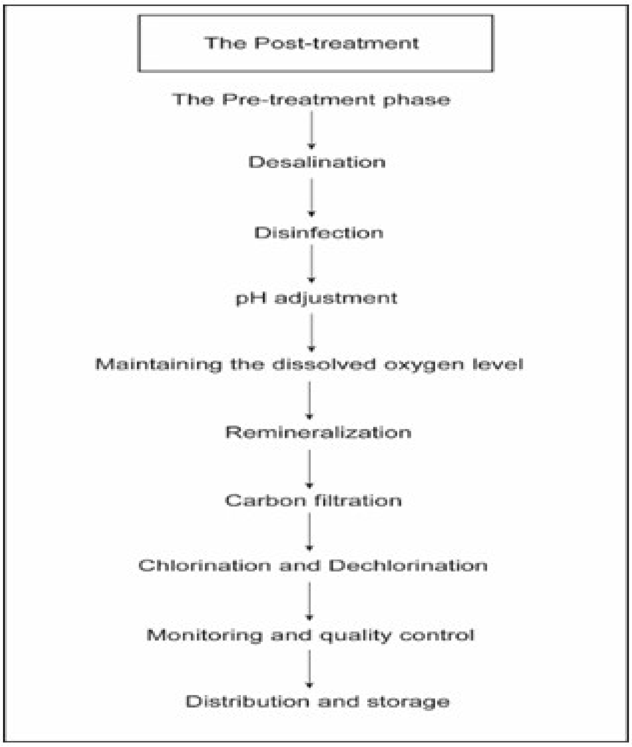

Figure 6: Schematic outline representing the different procedures involved in the post-treatment of water following desalination.

VI. CONCLUSION

To summarize, desalination holds immense potential to serve as a platform for freshwater production. The pre-water treatment, desalination, and post-water treatment are very effective in removing salts and other pollutants from water, as well as making water meet the standard quality for drinking water. However, to make this process more cost and energy-effective and to devise more environmental friendly brine disposal techniques, scientists, engineers, and financial consultants are working enormously. Taking this into account, we believe that desalinating the seawater is the hope of future generation to meet with the rapidly increasing demand of water.

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