

## Study of Ionic Migration in Sea Water through Directional Freezing

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**Summary:** The six most abundant ions present in seawater are chloride ( $\text{Cl}^-$ ), sodium ( $\text{Na}^+$ ), sulfate ( $\text{SO}_4^{2-}$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), and potassium ( $\text{K}^+$ ). By weight these ions make up almost 99 percent of the salinity of sea water. Removal of these ions or desalination makes the sea water useable. In the present work migration of these common and abundantly found ions in sea water has been studied when the water samples were subjected to directional freezing vertically as well as horizontally. Water samples collected from Arabian Sea were frozen in two partially insulated devices under different modes. The samples were placed in a freezer at different temperature conditions and all the six ions present in sea water were estimated in different fractions of ice extracted from various locations of frozen mass obtained after freezing. The fractions collected from the top of vertical device and from the periphery of the horizontal device were found to be completely decontaminated and free from the ions. Most of the ions were found concentrated at the bottom of the vertical device and in the center of horizontal device. The directional freezing method was found simple, inexpensive and free of chemicals method which can be effectively employed for the desalination of sea water particularly in the regions where cold energy is naturally available.

**Key Words:** Desalination; Directional Freezing; Decontamination of Sea water: Ionic Migration by Freezing.

### Introduction

The term desalination is usually referred to a treatment process that separates out the dissolved salts from sea water and makes the water useable for household. The techniques used for desalination can be categorized into two types. The first type desalination methods are those that involve no phase change at all. In such techniques, the extraction of water or salt takes place while the salts or pure water remain in the solution phase. These processes include: Reverse Osmosis (RO) and Electrodialysis (ED). The second type involves the methods that employ a phase-change process. In such plants, desalination takes place when water undergoes a phase change process either liquid to vapor (through boiling) or liquid to solid (through freezing). Techniques that are based on evaporation or freezing processes include: Multi-Stage Flash (MSF), Multi- Effect Distillation (MED), Vapor Compression Distillation (VC), Solar Humidification Desalination (SHD), Membrane distillation (MD) and Freezing-Melting process (FM) or Freeze Desalination (FD). Among the second category the techniques based upon evaporation are more commonly used, especially in the countries where cheap electricity is available as in the Gulf region. However, the desalination methods based on freezing, as being cost

effective, are slowly getting attention and popularity among researchers.

Removal of excess salts from the saline water by freezing is one of the oldest methods to purify water. This method of desalination, relies upon the principle that during slow freezing of water, the ice crystal structure cannot accommodate the impurities and excessive salts are rejected during phase transformation. In freezing process, ice crystals formed are made up of essentially pure water when latent heat is removed from saline water and thus lowering its temperature to its freezing point, because crystals exclude impurities from their structure as they grow. The desalination through freezing process has numerous advantages over thermal desalination processes such as low energy requirements, minimum corrosion potential and no scale formation on surfaces, and its suitability for remote areas, small communities, and cold regions, however it could not attract due attention and is not widely used commercially. Perhaps the greatest potential advantage of desalination by freezing is the very low energy requirement compared to that of the distillation processes [1]. The reduction in energy costs results because the latent heat of fusion of ice is only one-

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seventh the latent heat of vaporization of water. Separation of salts by freezing could save up to 90% of the energy required by the conventional thermal process. It is important to note that most of the conventional desalination methods have a significant environmental impact also in terms of seawater temperature and salinity. The brine discharge increases seawater temperature and salinity significantly [2].

For the last one decade a number of groups of workers have been studying different aspects of salt removal from saline waters [3-9]. Besides desalination, several researchers employed freezing technology for numerous applications mainly for the treatment of waste water [10-11]. Turkmen and colleagues used this method for removing heavy metal ions from waste water [12]. Freezing technology has also been employed for waste-activated sludge disruption [13]. Miia thoroughly investigated the separation efficiencies of freeze crystallization in wastewater purification [14]. Ottavio Franceschini worked on dewatering of sludge by freezing process [15]. Lorain and coworkers also investigated the Potential of freezing in wastewater treatment: soluble pollutant applications [16]. Patock investigated the influence of freezing water samples prior to chemical analysis [17]. Htira and coworkers used the technique for the treatment of industrial waste water [18]. Gao and his colleague employed freeze concentration method for the removal of five pharmaceutically active compounds from the waste water of a pharmaceutical industry [19]. They also used ice nucleation for the treatment of industrial effluents [20]. Gao and coworkers also examined the inactivation capacity of *E. coli* in waste waters by using natural freezing [21]. Same group of workers studied the removal of organic contaminants and toxicity from industrial effluents using freezing processes [22]. Our group also studied the migration of ions and gases in aqueous solutions under directional freezing [23, 24]. Directional freezing was also employed for separation of the bacterial contamination from aqueous medium and concentration of enzymes [25, 26].

In the present work we collected sea water from Arabian Sea and proceeded it through two modes of directional freezing in two partially insulated devices. In both cases the dissolved ions migrated along the freezing front and concentrated in the center of horizontal device and at the bottom of the vertical device. This approach has adequate potential not only for decontamination of polluted waters but also can be used for preconcentration and as a separation technique in analytical chemistry.

## Experimental

*Collection of Sea Water Samples:* Sea water samples were collected in plastic cans from 3, 5, 7 and 10 Km inside of Arabian Sea from Karachi beaches. To remove any suspended contamination the samples were filtered through filter paper. As shown in Table 1, when all the four samples of sea water were analyzed for sodium, potassium, calcium, magnesium, chloride and sulphate, no significant difference in the concentration of ions was observed in the samples collected from different distances from the beaches in Karachi. To prepare a representative sample, all the four samples were mixed in equal proportions and the resultant mixture was analyzed for sodium, potassium, calcium, magnesium chloride and sulphate ions. The concentration found for each ion was taken as standard concentration of that ion in sea water used in this work.

*Instrumentation for Estimation of ions:* Sodium, potassium and calcium in sea water samples as well as (after freezing) from ice samples were estimated with the help of a Flame Photometer. A Corning Flame Photometer Model 410 equipped with original filters was used for this purpose. Standard solutions of the metal ions were also provided by the manufacturer. Magnesium was estimated with the help of Xplora model Atomic Absorption Spectrophotometer of GBC Company equipped with Air/Acetylene flame and magnesium hollow cathode lamp. Chloride and sulphate were estimated with the help of Ion Selective Electrode system. Ion Selective Electrode System of EDT Instruments and electrodes of same company were used for the measurement of chloride and sulphate.

*Radial Device:* Horizontal or radial device used in these studies was a stainless-steel bowl of approximately 2-liter capacity, 18-inch diameter and 5-inch depth. After adding the sea water, the bowl ice was effectively insulated from top and the bottom with the help of insulated foam and tape so that the heat could be transferred through sides only and the freezing front should move from periphery to the center of the bowl. After sealing with insulated tape, the device was placed in a deep freezer at different temperature conditions (from -4°C to -18°C) for different intervals of time (12 to 24 hours).

*Vertical Device:* Vertical device was an 18-inch long and of 4-inch diameter PVC pipe of 3mm thickness. One end of the pipe was completely sealed with the help of a thick plastic disc. The jar type device was further insulated from sides and bottom with the help of tape and insulating foam so that heat could transfer from the top only and the freezing front could

move from top to bottom. After filling with sea water up to one inch distance from the brim, the device with one end open was placed inside of a deep freezer at different temperature conditions (from -4°C to -18°C) and for different intervals of time (12 to 24 hours).

*Extraction of Ice Samples:* After a certain time, interval, the devices were removed from the freezer and frozen mass was taken out from them by applying warm water outside the devices. Ice samples were extracted from different locations of the frozen mass obtained from devices and preserved in clean flasks for analysis. From the ice obtained from radial device, five aliquots were extracted, with the help of a cork borer type gadget, between the center and the periphery. The bar type mass obtained from vertical device was cut down with a warm knife into ten equal sized slices and aliquots were transferred into cleaned flasks. Sodium, potassium and calcium were estimated from each fraction by flame photometry while magnesium was determined by atomic absorption spectroscopy. Both anions, chloride and sulphate were estimated with the help of Ion Selective Electrode system. The results are shown in Figures 2 to 6.

**Results and Discussion**

*Sea Water Composition:* Sea water samples were collected from offshore locations of Arabian Sea up to 10 Km away from Karachi beach. The analysis of sea water samples showed a bit higher result of each ion than reported in a previous publication [27]. This increase in the concentration of ions may be due to the salts contributed by rivers in last ten years or due to some seasonal variation. As there was no significant difference in the concentrations of sodium, potassium, calcium, magnesium, chloride and sulphate in different samples, as revealed by Table-1, a representative sea water sample was prepared by thoroughly mixing all the water samples. The ionic composition of the representative sea water sample is shown in Fig. 1.

*Radial Freezing:*

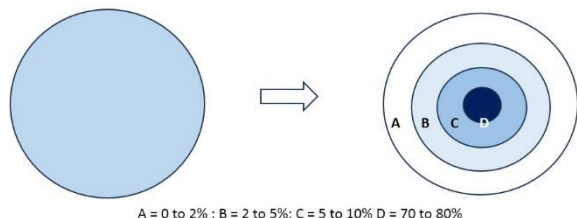


Fig. 1: Total salt (NaCl) distribution after Radial Freezing.

As shown in Fig. 1, after the radial freezing when the aliquots of ice were analyzed from varying distance from the center, it was found that more than 80% salt (NaCl) was concentrated in the inner most circle having a radius less than the one sixth of the radius of the device. Ice fraction from circle A was almost free from the salt, aliquot from B contained not more than 5% of the total salts present in the bowl, ice portion from C was contaminated up to 10% while rest of the salts were concentrated in the center. In one of our similar experiments done previously with  $KMnO_4$ , the outer rim was found completely free from  $KMnO_4$  [23]. These results are also in line with the model reported by Badawy [9]. As shown in Figs. 3 to 7, all the ions present in sea water showed almost similar behavior when subjected to radial freezing. Every ion, up to 80% of its concentration was concentrated in the center.

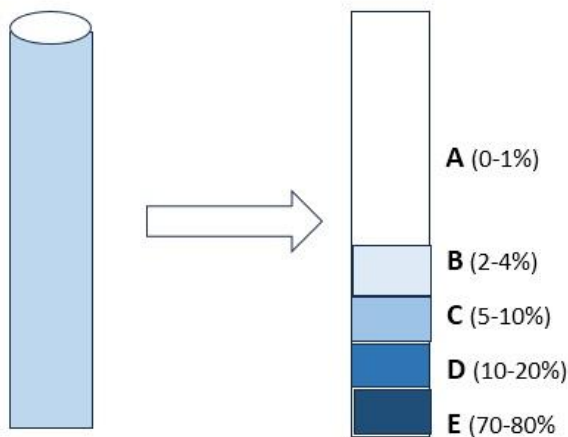


Fig. 2: Total (NaCl) distribution after Radial Freezing.

*Vertical Freezing:* The frozen mass obtained from vertical device was cut into ten equal sized slices. The upper six slices were almost free from salts while the 98% salts were distributed into lower four slices. The lowest one contained 70 to 80% of the total salt present in the sea water contained in the device. The salt concentration decreased abruptly in the second and third slice from the bottom. The fourth slice contained not more than 5% of the total salt. In case of vertical freezing, it was noted that diameter/length ratio of the device also affected the separation of dissolved contents. Best separation was obtained when the ratio of diameter/length was 0.22.

*Time and Temperature Factors:* Time and temperature are two important factors which affect the salt separation by radial as well as vertical directional freezing significantly. In both modes, the sea water

sample was subjected to directional freezing at three different temperatures -4°C, -10°C and -18°C (by setting deep freezer controls). At the lowest temperature water in both the devices was completely frozen in less than 12 hours whereas when controls were set at -4°C, it took 20 to 24 hours for complete freezing. In both cases the salt separation occurred at relatively higher temperature (-4°C) and in maximum time (24 hours) and was significantly better than that which took place at coldest temperature (-18°C) in 10 hours.

*Separation of Individual Ions:* All the six ions sodium, potassium, calcium, magnesium, chloride and sulphate present in sea water almost behaved similarly. Migration of various ions is shown in Fig. 4 to 7. In radial freezing using optimum conditions of time and temperature (minimum temperature and maximum time) more than 90% salts got migrated to the center of the device. Three inches ring along the periphery was free from any contamination. In vertical freezing more than 90% ions were collected in couple of inches close to the bottom of the device. The upper half of the device was completely free from the ions. By rough estimates we can safely say that by using optimum conditions of time, temperature and geometry of the device we could completely decontaminate 60% of the total volume of saline water taken for the experiment.

**Conclusions**

From the present and previous work in this field it can be safely concluded that directional freezing has sufficient potential to desalinate the sea water by using far more less energy as compared to any thermal method of desalination. This technique can be effectively used for decontamination of water in the countries where natural cold energy is abundantly available. The technique can also be employed for preconcentration and separation of enzymes and bacteria [14, 15]. In Pakistan there are many areas in the north of the country where clean water is still a problem but natural cold energy is abundantly available and sub-zero temperature is very common in most part of the year. This technique could be useful for decontamination of water from rivers and lakes and for the treatment of industrial effluents.

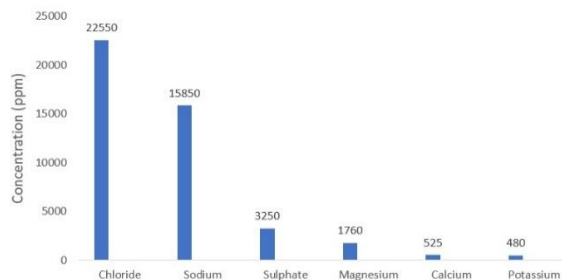


Fig.3: Ionic Composition of Sea water.

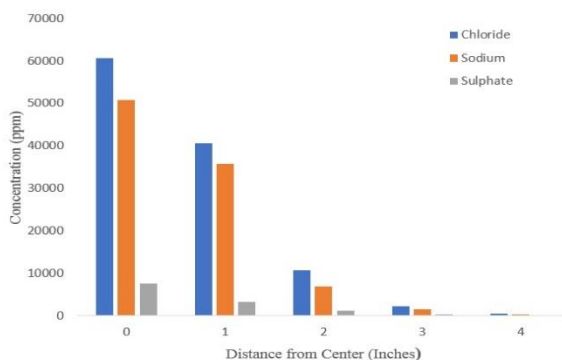


Fig. 4: Radial Migration of Chloride, Sodium and Sulphate.

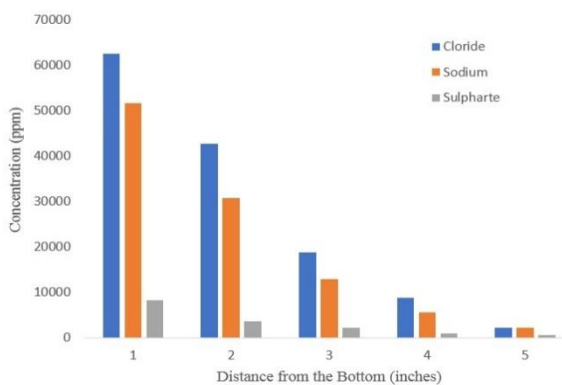


Fig. 5: Vertical Migration of Chloride, Sodium and Sulphate.

Table-1: Ionic concentration (ppm) of Sea Water of Arabian Sea taken from different distances from beach.

Sample No. (Dist. from Beach)	Chloride	Sodium	Sulphate	Magnesium	Calcium	Potassium
A (3 Km)	22555	15855	3252	1750	515	475
B (5 Km)	22540	15852	3245	1765	525	482
C (7 Km)	22560	15850	3250	1760	530	485
D (10 Km)	22550	15845	3250	1762	522	480
Mean ± S.D	22551±8.5	15852±2.21	3249±2.9	1759±6.5	523±6.6	480.5±4.2

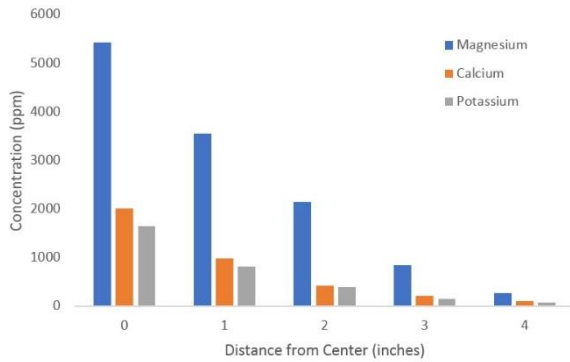


Fig. 6: Radial Migration of Magnesium, Calcium and Potassium.

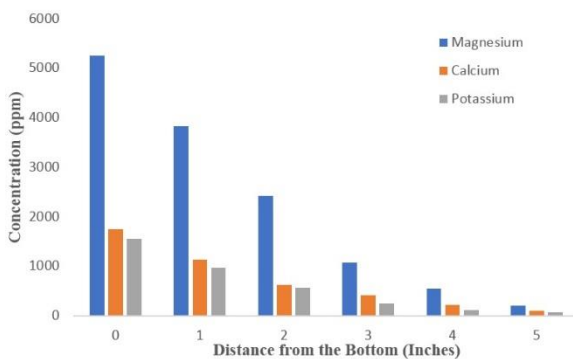


Fig. 7: Vertical Migration of Magnesium, Calcium and Potassium.

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