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Laboratory freezing desalination of seawater

Sayed M. Badawy[a,b]

[a]*Faculty of Science, Chemistry Department, Aljouf University, Sakaka, Saudi Arabia, email: sayedbadawy@hotmail.com*
[b]*Faculty of Medicine, National Center for Clinical and Environmental Toxicology, Cairo University, Cairo, Egypt*

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ABSTRACT

Freeze desalination of samples of seawater from Umluj beach, Red Sea, in Saudi Arabia, was investigated by laboratory experiments using nondirect freezing. The influence of kinetic parameters including degree of crystallization, freezing–melting cycles, and gradual melting on the total dissolved solids (TDS) and salt rejection was examined. The melted ice water produced by partial crystallization of single-stage freezing has two times less salt concentration than the feed seawater (TDS, 40,916 mg/l). Continuous cycling of the freezing–melting process reduced the dissolved salts to 1.5% with TDS 610 mg/l, in the level of drinking water. The TDS of the melted ice decreased with gradual melting time and reached 693 mg/l after 6 h. The results indicated that the laboratory freezing desalination could decrease sea ice salinity from 4.1 to 0.06% without using chemical additives.

Keywords: Seawater; Freezing; Desalination; Salt rejection; TDS

1. Introduction

Many countries in the world suffer from a lack of natural freshwater, and the vast majority of people will live with severe pressure on freshwater within two generations, due to pollution, climate change, and excessive use of resources [1]. Desalination of seawater will be our best choice. Oceans represent the major water reservoir. About 97% of the earth's water is seawater [2,3].

Many types of seawater desalination systems such as multi-stage flash evaporator, vapor compression distillation, multiple-effect distillation, reverse osmosis, and freeze desalination were introduced for production of freshwater from seawater [4]. The technique of freezing has been proposed as an alternative for desalination in several studies [5]. Desalination by freezing is based on the fact that ice crystals are essentially made up of pure water. During the process of freezing, dissolved salts are excluded during the formation of ice crystals resulting in separation of ice and brine [6]. The major types of freezing–melting process include direct contact freezing, vacuum freezing, indirect contact freezing, and eutectic separation [7].

Freeze desalination has some advantages in comparison with other methods such as its energy consumption, scaling, and corrosion resistance because of the low operating temperature and no discharge of toxic chemicals to the environment [7,8]. However, there are some mechanical problems with ice handling [8]. A small number of plants have been built over the past 40 years, but the freezing process has not been commercialized successfully to produce freshwater for municipal purposes [5].

In the present study, the freeze desalination of samples of seawater from Umluj beach, Red Sea, in Saudi Arabia, was investigated for obtaining the drinkable water by batch experiments in a laboratory scale. The influence of kinetic parameters including degree of crystallization, freezing–melting cycles, and gradual melting on the total dissolved solids (TDS) and salt rejection was studied.

2. Experimental methods

2.1. Freezing of seawater

The sea water samples with TDS of 40,916 mg/l were taken from Umluj beach, Red Sea, in Saudi Arabia. The freezing of seawater in 1.6 L ice cubes with a degree of crystallization of 75–100% was achieved by nondirect contact using an external cooling in the freezer (−10℃) at different freezing time, 6–10 h.

2.2. Freezing–melting cycles

The experimental steps used for the laboratory desalination by freezing–melting batch process are as follows: (a) freezing of seawater with a degree of crystallization of 75–85%, (b) separation of salts by draining of brine water and surface washing of adhering salts by tap water, (c) melting of sea ice in a 5-L glass beaker on hot plate up to room temperature, and (d) repeating the previous steps of freezing–melting cycling until obtaining drinkable water (Fig. 1).

2.3. Gradual melting

The experimental steps used for the laboratory desalination by freezing and gradual melting are as follows: (a) freezing of seawater with a degree of crystallization of 75–100%, (b) draining of brine water without surface washing, (c) sweating or gradual melting at room temperature of the ice layers, and (d) separate the melted waters at interval times until obtaining drinkable water under the effect of temperature gradient (Fig. 1).

2.4. Measurements

The TDS (TDS mg/l) were measured by calibration with a conductivity of standard solutions of KCL from 0 to 50,000 mg/l (Fig. 2), according to Standard Methods for the Examination of Water and Wastewater, 1999 [9]. The electrical conductivity of the samples

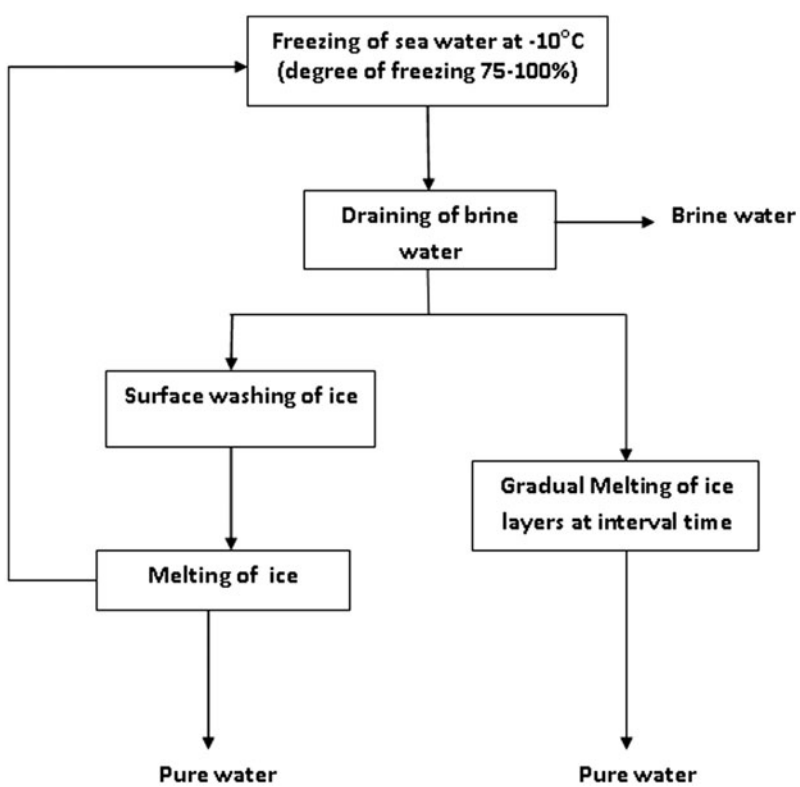

Fig. 1. Desalination by (a) melting–freezing cycling and (b) gradual melting.

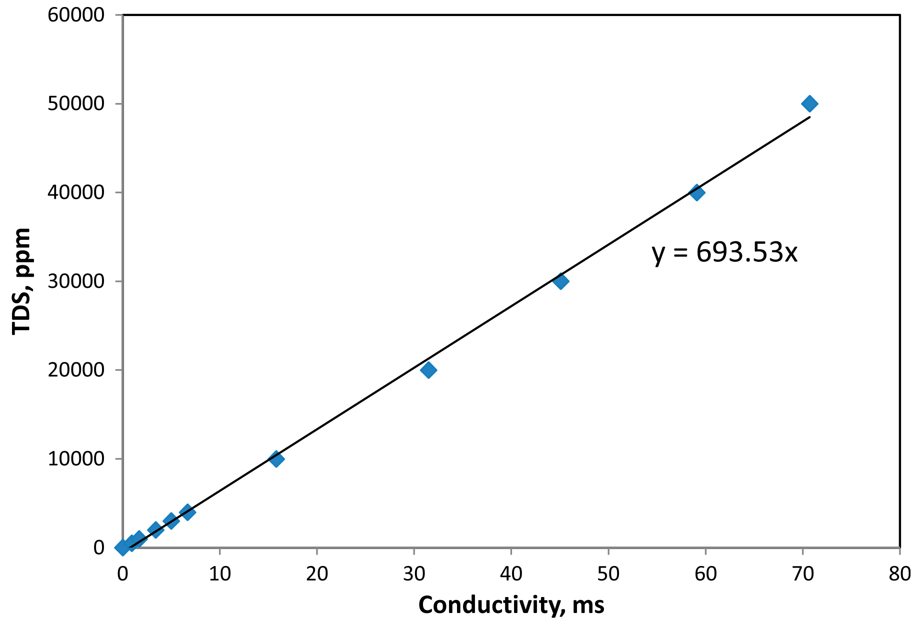

Fig. 2. Calibration curve of TDS vs. conductivity.

was measured at 25°C with a conductivity meter (HANNA EC215). The salt rejection was calculated by the formula as follows:

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \quad (1)$$

where C_P is the TDS of the produced melted water of sea ice (mg/l), and C_F is the TDS of feed seawater (mg/l). The loss factor is as follows:

$$L = \left(1 - \frac{m_P}{m_F}\right) \times 100\% \quad (2)$$

where m_P is the mass of the produced melted water of sea ice (kg), and m_F is the mass of feed sea water (kg). The degree of crystallization is as follows:

$$R_F = \frac{V_p}{V_F} \times 100\% \quad (3)$$

where V_F and V_P are, respectively, the initial volume of feed sea water (L) and volume of the produced melted water of sea ice water (L).

3. Results and discussion

Freezing desalination processes are based on the fact that ice crystals are made up of essentially pure water when the temperature of saline water is lowered to its freezing point and further heat is removed [10]. Typical binary phase diagram of salt water (Fig. 3) shows the temperature–composition fraction of NaCl relationships among the different phases of the salt water. For a binary solution of 4% NaCl, which is the salinity of the seawater samples in this study, water starts to transit from the liquid phase to the solid crystal phase when the temperature is decreased and lower than the freezing point. During the transition, the salts are rejected by the regularly packed ice crystals of high water purity [11,12]. Continuous freezing has major potentials for salt rejection and brine

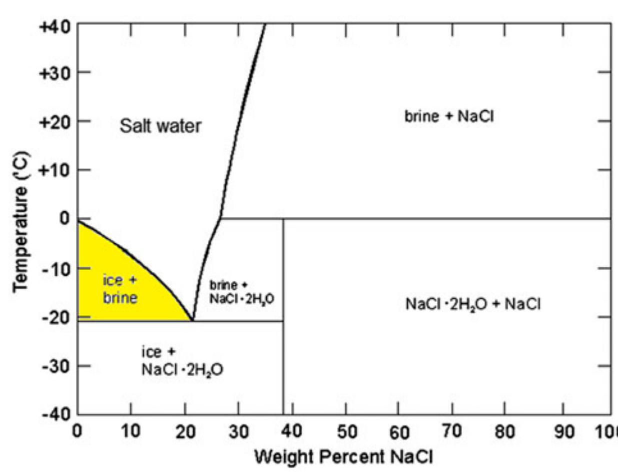

Fig. 3. Phase diagram of salt water.

disposal. The desalination process of seawater could be achieved by freezing and melting technique via controlling the kinetic parameters such as degree of crystallization, freezing–melting cycling, and gradual melting.

3.1. Degree of crystallization

In the process of freezing, the dissolved salts are rejected during the formation of ice crystals leading to a separation of ice and brine. As ice grows at the eutectic point, salt ions are rejected from the ice. The salt builds up an interface; salinity of a thin layer of a few millimeters in thickness, which could be removed in the wash step [13].

Desalting of seawater could be achieved in three steps: (1) freezing step, leading to the crystallization of the ice layers, (2) draining the brine water during washing, and (3) then melting step.

Fig. 4 shows the effect of degree of crystallization on the salt concentration of both the melted ice and the brine water. The melted ice water produced by single freezing–melting process has two times less salt concentration than the feed seawater (40,916 mg/l), whereas the brine water has two times more salt concentration than the feed. As the degree of crystallization increases from 75 to 87%, TDS of the melted ice increase from 18,932 to 22,192 mg/l and TDS of the concentrated brine water increase from 80,654 to 106,799 mg/l. The salts dissolved in seawater are not incorporated into the ice crystal lattice, so their concentration in the remaining brine increases and the flow of salt ions is retarded by the dynamic fluid viscosity. On the other hand, the ice may develop pores that are disconnected from regular fluid motion and therefore retain their salt content until the melt [13].

Partially freezing makes it possible to obtain a brine liquid phase, which is charged in solute and a solid phase which is composed of ice being able to become freshwater by (a) continuous freezing–melting cycles or (b) gradual melting method, which consists of purifying in depth the ice layers by melting of the impure zones.

3.2. Freezing–melting cycles

Figs. 5 and 6 shows the effect of freezing–melting MF cycling on the salt rejection of seawater at different freezing time and sizes of ice cube, respectively. At the first freezing–melting cycle of the feed seawater (TDS 40,916 mg/l), the salt rejection is 29% with TDS 28,017 mg/l. After the fourth freezing–melting cycle, the salt rejection improved to 84% with TDS 6,584 mg/l. The brine is trapped between the lamellae of the ice, allowing for a retention of 71% of the dissolved salts in the sea ice after the first MF cycle and 16% after the fourth MF cycle.

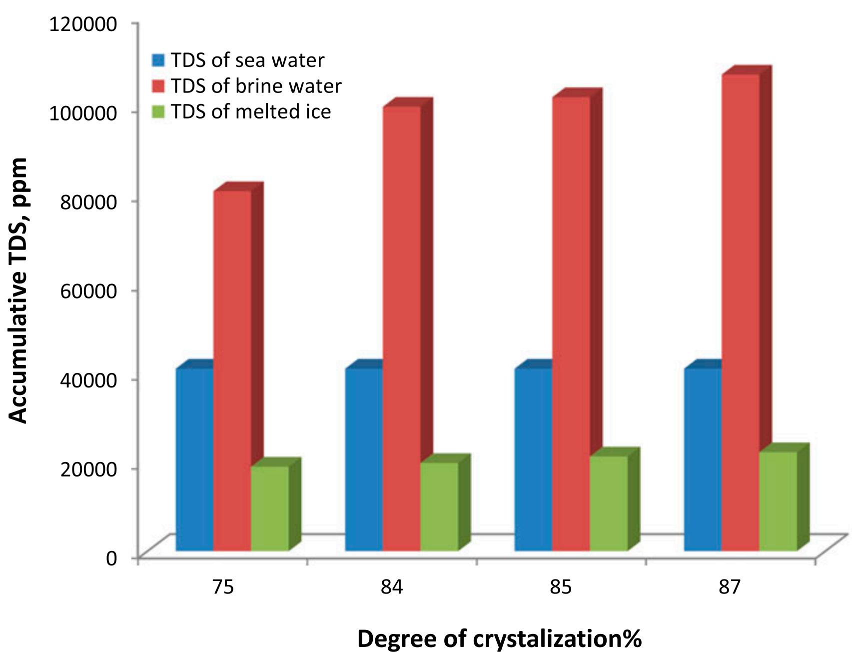

Fig. 4. Effect of degree of crystallization on the salt concentration of both the melted ice and the brine water.

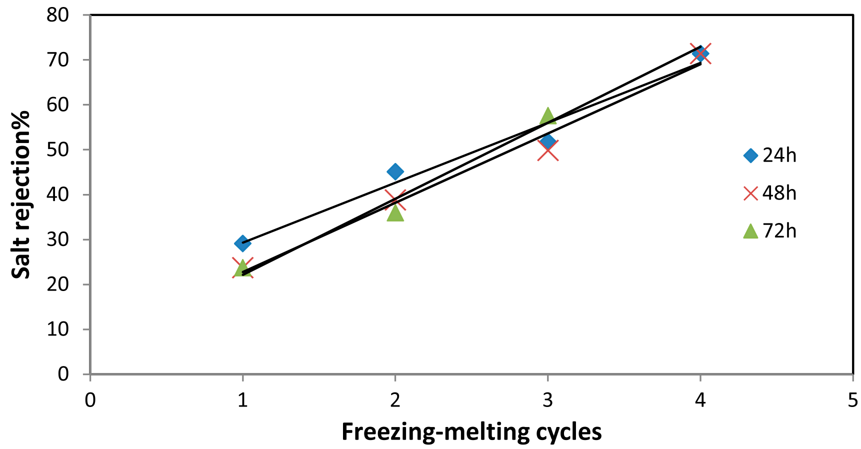

Fig. 5. Effect of number of freezing–melting cycles on the salt rejection of seawater at different freezing time.

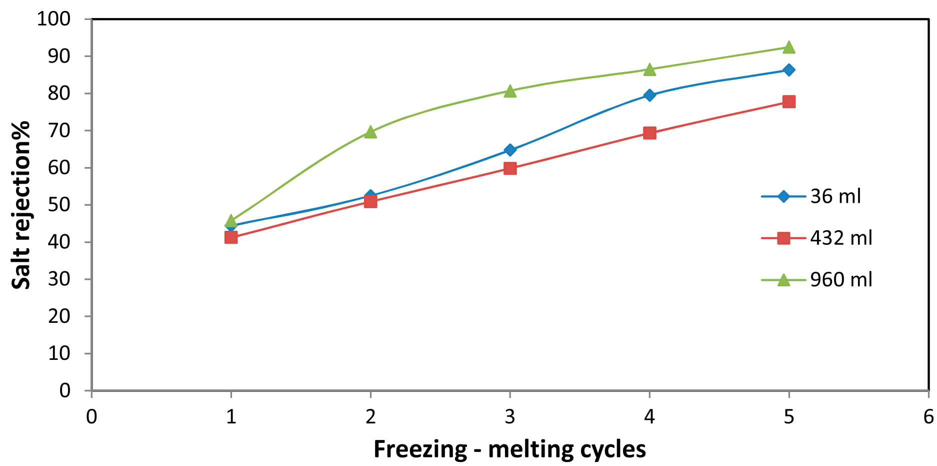

Fig. 6. Effect of number of freezing–melting cycles on the salt rejection of seawater at different sizes of ice container.

Frozen sea ice contains brine pockets i.e. highly saline water trapped in the ice during the process of freezing [7]. For completely desalting of seawater to obtain drinkable water, the freezing–melting cycles should be continued.

Continuous cycling of freezing/washing/melting process reduced the dissolved salts to 1.5%, i.e. salt rejection 98.5%, after the eighth FM cycle with TDS 610 mg/l, in the level of drinking water according to WHO.

The mass loss is high when the purity is high due to draining off the concentrated brine water in the washing step. The mass loss increased from 18.6% after the first FM cycle to reach the maximum mass loss of 66% after the eighth FM cycle, whereas the salinity of the melted ice decreased from 25,017 to 610 mg/l, as shown in Fig. 7.

3.3. Gradual melting (sweating)

Gradual melting is an efficient method by which ice layer is purified under the effect of temperature gradient [14]. The brine inclusions enlarge upon warming during the melting at room temperature and form new pathways for brine and melt water flushing, leading to desalination throughout the ice [13]. Any temperature change affects the pore microstructure of the ice as well as the salinity and chemical composition of the brine.

The desalting of the sea ice could be continued through gradual melting/sweating and separating the salts into a smaller volume at different time intervals. The rejection of the brine included in the ice layer is induced by the temperature gradient and allows purification of the ice layers during crystallization [15].

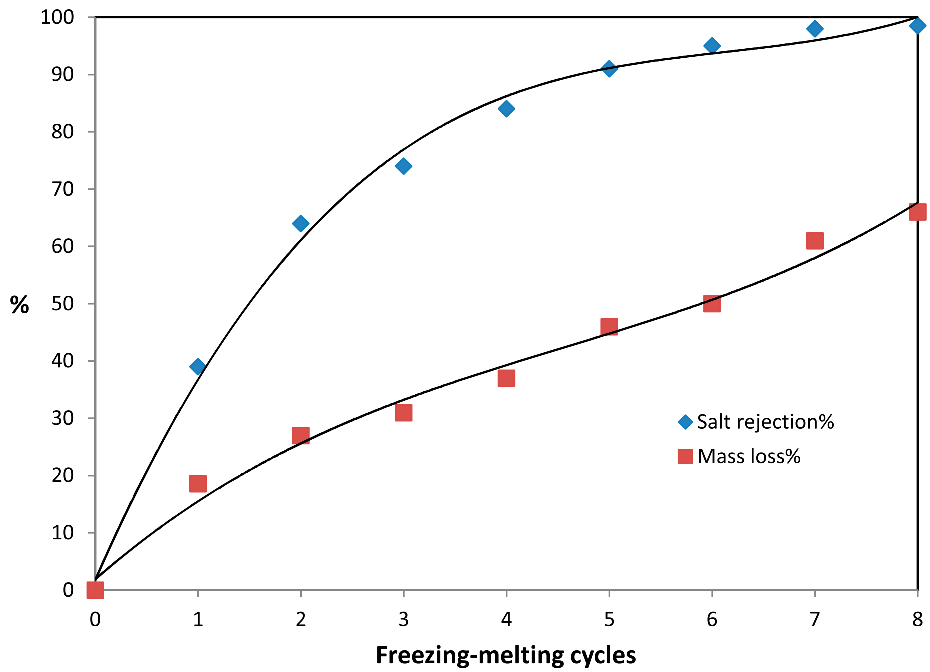

Fig. 7. The mass loss % and salt rejection % with FM cycles.

Fig. 8 shows the effect of melting time on the salt rejection for samples of different degree of initial freezing. The salinity of the melted ice decreases with melting time at room temperature. In case of complete freezing (100% freezing), the ice layers melted to give brine concentrated water with negative salt rejection ranged from −88.42% (TDS 74,482 mg/l) at 1 h to −10% (TDS 43,482 mg/l) at 3 h. The remaining ice

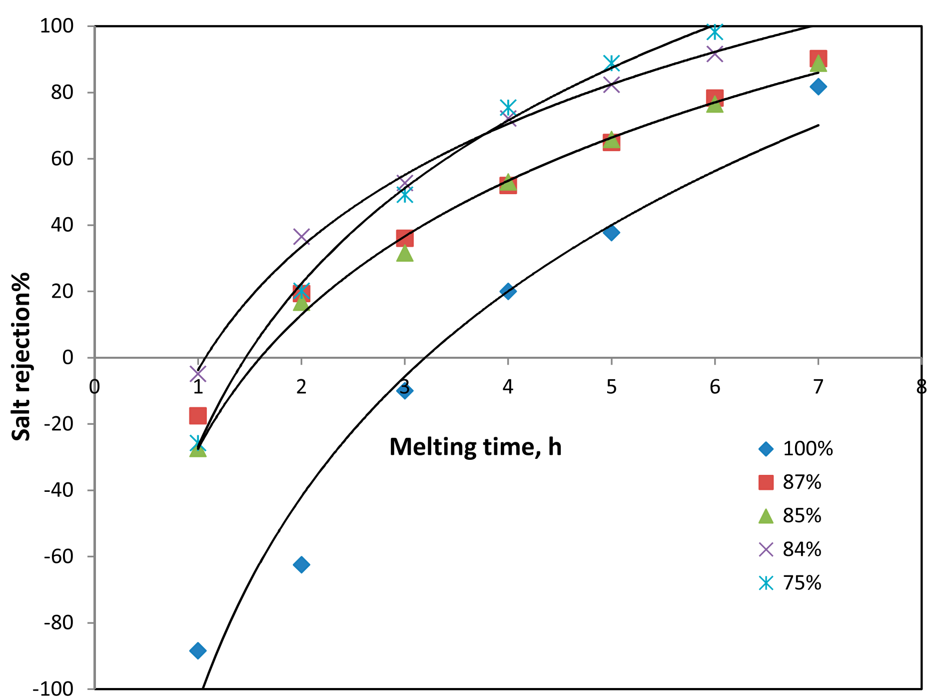

Fig. 8. Effect of melting time on the salt rejection of melted ice for samples of different degree of initial freezing.

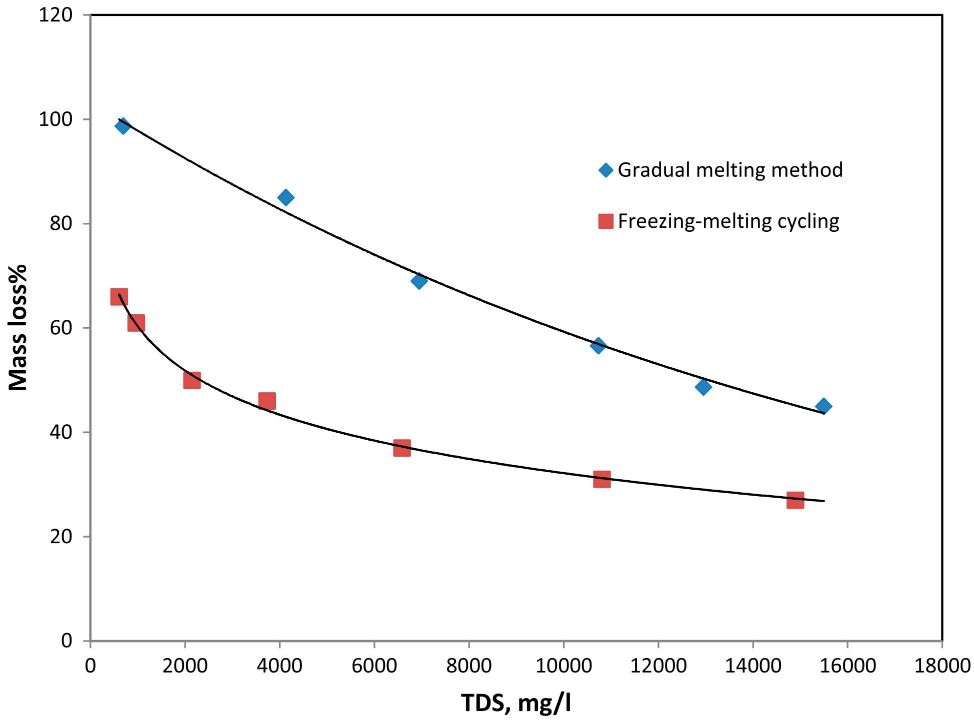

Fig. 9. Mass loss % vs. TDS of the melted ice.

melted to give water with positive salt rejection ranged from 20% (TDS 31,623 mg/l) at 4 h to 81% (TDS 7,212 mg/l) at 7 h.

At the partially freezing (75% freezing), the ice layers melted to give brine water with negative salt rejection of −25.79% (TDS 49,724 mg/l) at 1 h. The remaining ice melted to give water with positive salt rejection ranged from 20% (TDS 31,554 mg/l) at 2 h to 98.23% (TDS 693 mg/l) at 6 h.

Fluid moving though the ice experiences a resistance that is due to both microscopic obstacles in the flow path and viscous drag along the pore walls [13]. As the sample is warmed at room temperature, the brine volume fraction increases. The size, morphology, and connectivity of pores evolve, with pores visibly linking up at warmer temperatures. The X-ray microtomography in a previous study showed how sheets of brine segregate into disjunct, isolated pores at low temperatures and how they start to link up at higher temperatures [16].

The total time of desalination of one freezing stage in laboratory scale takes about 6 h for freezing at −10˚C plus 6 h for gradual melting at room temperature, to reach drinking water, with unfortunately, mass loss of about 98%.

Fig. 9 shows the comparison between the mass loss% vs. TDS by using FM cycling and gradual melting methods. The mass loss of FM cycling method reached 66%, while the mass loss of gradual melting method reached 98%.

The results indicate that the methods of freeze desalination could decrease seawater salinity of Umluj beach from 4.1% (TDS 40,916 mg/l) to 0.06% (TDS 610 mg/l) without using chemical additives. The disadvantages of these methods for commercial desalination of seawater, such as formation of salt pockets between ice layers, mass loss, and mechanical ice handling will be investigated in the future work.

4. Conclusion

Freeze desalination of samples of sea water from Umluj beach (TDS 40,916 mg/l), Red Sea, in Saudi Arabia, was investigated by laboratory experiments using non-direct freezing. The influence of kinetic parameters including degree of crystallization, freezing–melting cycles, and gradual melting on the TDS and salt rejection was examined. The melted ice water produced by controlling degree of crystallization of single-stage freezing has two times less salt concentration than the feed seawater, whereas the brine water has two times more salt concentration than the feed. Continuous cycling of the freezing–melting process reduced the dissolved salts to 1.5%, i.e. salt rejection 98.5%, at the eighth cycle with TDS 610 mg/l, in the level of drinking water according to WHO. The dissolved salts TDS of the melted ice decrease with the gradual melting time and reached 693 mg/l after 6 h. The results indicated that the freeze desalination could decrease seawater salinity from 4.1% (TDS 40,916 mg/l) to 0.06% (TDS 610 mg/l) without using chemical additives.

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