Effects of Halide Anions on Water Desalination Based on Crystallization Methods: Freezing and Tetrahydrofuran Hydrate Formation

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ABSTRACT: *In this study, water desalination was performed using the freezing method and Tetrahydrofuran hydrate formation in a stationary reactor. The experimental setup includes two coaxial cylinders, in which ice crystals deposit outside the cool inner cylinder; thus the salt concentration increases in the residual brine. In order to evaluate the performance of these methods, the removal percentage of salt was measured by the electrical conductivity instrument. The results show that the removal efficiency decreases with an increasing salt concentration in the freezing method while a different trend is observed in the hydrate formation method. As an important result, the salt removal efficiency of the hydrate formation method was higher than the freezing process. Also, to investigate the effect of the anionic size on the salt removal efficiency, the experiments were performed with NaCl, NaBr, NaF, and NaI, which have the same cations. The results show that the performance of desalination improves by increasing the anionic radius. So the dissolved mineral components are removed in the following order: $I^- > Br^- > Cl^- > F^-$. The removal of salts of a higher size is further by hydrate-based and freezing desalination.*

INTRODUCTION

Water is the basic substance of life on earth, and it is increasingly in short supply due to the increased population and industrial expansion in developing countries [1,2]. Hence significant attempts have been performed to develop desalination methods [3,4] besides the traditional technologies for providing a water source from the brine water [5,6].

Generally, desalination technologies can be categorized into two types. The first type of plant is those that involve no phase change such as Reverse Osmosis and Electrodialysis process. The second type plants of water desalination involves a phase-change process including Multi-Stage Flash, Multi-Effect Distillation, Vapor Compression Distillation, and Freezing- Melting [7].

In recent years, one of the investigated developing technologies is the crystallization process including the freezing and the gas hydrate methods for desalination. The concept of freezing desalination was initially presented in 1950 [8] and then various attempts have been made to improve its efficiency. For example, *Karnofsky et al.* [9] and *Wiegandt et al.* [10] conducted experiments in this field. In this process in which water is changed to ice

and separated from brine, water with a high concentration of salt can be removed, and then by melting the ice, freshwater is obtained. The different types of freezing systems are direct, indirect, and vacuum freezing [7]. The advantages of the freezing technique have been given as an alternative for seawater desalination, the purification of mixtures [11,12], wastewater treatment [13,14], and food liquid concentration [15].

Mandri et al. performed the seawater desalination process based on the indirect freezing in water–NaCl solutions (35 g/kg of NaCl). They studied the effective kinetic parameters such as initial concentration of ice, sweating temperature, and sweating time by experimental design [2]. Also, the results generated by *Rich et al.* indicated the feasibility of the freezing and sweating steps with good operating conditions to produce drinking water [3]. They developed a dynamic layer crystallizer with samples of seawater from Nice, Rabat, and Marseille and NaCl solutions and reached salinities lower than 0.5 g/kg, satisfying the standards of drinking water. *Williams et al.* assessed an ice maker machine for desalting brines by Freeze desalination; influencing the different parameters of separation performance [4]. *Kayansayan* and *Acar* studied the ice freezing around a finned tube [16]. Also, *Jang et al.* studied freezing desalination to obtain the ice-quality and productivity enhancement [17]

Clathrate hydrates are crystalline solid compounds, composed of hydrogen-bonded water molecules and some other gas (or liquid) species [18,19]. The hydration methods have been studied for desalination of seawater during the past 50 years considering the capability of gas hydrates to form a solid substance consisting of distilled water and hydrate former [20,21]. In 1940, gas hydrate formation was proposed as a novel method to produce potable water from seawater, and in the 1960 and 1970, considerable attention was continued. In the United States, many companies used this method on a pilot plant scale [22]. In 1996, *Ngan* and *Englezos* investigated the process of nucleation, growth, separation, and melting through propane hydrate formation in NaCl solutions (2.5 wt %) [23]. In 2003, *Javanmardi* and *Moshfeghian* compared a unit seawater desalination based on the hydrate formation with other methods [24]. *Park et al.* accomplished hydrate-based desalination with a novel apparatus design to extract the dehydrated gas from the hydrate slurries in a new reactor. Moreover, they suggested different hydrate

formers such as refrigerants for further desalination research [5]. Some researchers worked on the removal efficiency in presence of different ions. *Lu et al.* reported that cation and anion play different roles in inhibiting hydrate formation and gas hydrate stability conditions [25]. *Mohammadi et al.* investigated the methane hydrate phase equilibrium in the presence of NaBr, KBr, CaBr$_2$, K$_2$CO$_3$, and MgCl$_2$ aqueous solution. The new experimental data for methane hydrates in MgCl$_2$ aqueous solution with 0.1 mass fraction were compared with some selected data from the literature and the agreements were found acceptable [26]. In 2014, *Lee et al.* used CH$_4$ and CO$_2$ as guest gases in the HBD process. In this work cations such as Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, and B^{3+} and anions Cl$^-$ and SO$_4^{2-}$, were investigated respectively and high removal efficiency was shown for CO2 as a guest gas [27]. In 2014, *Sowa et al.* studied the effect of nine-strong monovalent salts in a wide range of concentrations on the formation of ice, Tetrahydrofuran (THF), and methane/propane mixed gas as hydrate formation. The results showed that sufficiently concentrated (>1 M) salt solutions act as thermodynamic inhibitors. However, at lower concentrations, salts may play a promoter or inhibitor role in hydrate formation [28]. In 2014, *Farhang et al.* reported a similar kinetic promotion effect for dilute sodium halide solutions during CO$_2$ gas hydrate formation. In this research transition from promotion to inhibition effects of CO$_2$ hydrate formation were observed somewhere between 10 and 100 mM of sodium halide solutions [29].

Herri et al. presented a systematic review of the past developments of the Hydrate-Based Desalination process using cyclopentane as hydrate guest. They found when compared to traditional applications, the cyclopentane hydrate-based desalination process could be a promising solution [30]. *Song et al.* studied hydrate–based desalination to obtain high water recovery and purity. They examined the desalination and Li$^+$ enrichment performance by using single-stage desalination *via* cyclopentane hydrate formation in brine solutions of LiCl, LiBr, and LiI with concentrations ranging from 0.01 to 0.6 mol/L. They found the halide ions have different capabilities, with an order of Cl$^-$<Br$^-$<I$^-$ and also, the water recovery of 40% can be obtained in 1 hour of reaction [31]. *Kang et al.* investigated Salt removal *via* cyclopentane gas hydrate formation. They carried out the experiments at 277.15 K, using seawater of 3.4 wt% salinity and

3 mol%cyclopentane to the water-cyclopentane mixture. The single-stage hydrate formation followed by filtration removed 63% of the salt ions while the salt removal was improved by washing treatment to nearly the same degree regardless of the kind of salt ions and the salt removal efficiency improved up to 42% more than that of filtration only [32]. *Koh et al.* studied the role of crystal nucleation and the growth of gas hydrates in water desalination. They found that the induction times decrease with increasing subcooling, and also the hydrate memory effects are reduced with increasing replenish time [33].

Karamoddin and *Varaminian* investigated the hydrate growth process of HCFC141b refrigerant in different brine solutions to desalinate the saline water [34]. They also designed a new apparatus for hydrate formation in high pressure for water desalination experiments [35]. They investigated the potential of crystallization technologies containing the freezing method and process of gas hydrate formation for water desalination processes in the newly designed apparatus. For this purpose, the component of tetrahydrofuran was used as a hydrate former and the brine solutions were supplied from salts of NaCl, KCl, CaCl$_2$, MgCl$_2$ and also Caspian seawater. According to the obtained results, the water desalination process based on hydrate formation requires lower cooling to provide the required driving force besides the higher efficiency [36].

The component of tetrahydrofuran is in the liquid phase and forms the structure II of hydrate, besides the structure II of hydrate contains more water molecules; so this hydrate former is selected in the hydration experiments. The main purpose of this research is the comparison of water desalination efficiency by using freezing and gas hydrate methods in a static layer crystallizer. The desalination experiments were performed with ice and hydrate layers produced from brine solutions in presence of NaF, NaCl, NaBr, and NaI salts. The results showed that the desalination efficiency depends on different factors such as the salt concentration, ionic radius of salts, and type of crystallization process; hydrate formation or freezing

EXPERIMENTAL SECTION
Materials
Tetrahydrofuran as hydrate former (THF) and salts were purchased from Merck Company purity of them is summarized

Table 1: Purities and suppliers of the materials studied.

Chemical	Supplier	Purity (%)
THF	Merck	99.5
NaCl	Merck	99.5
NaBr	Merck	
NaF	Merck	99
NaI	Merck	
H$_2$O	–	Deionized

in Table 1. Also, De-ionized water was used in all experiments.

Apparatus
The experiments were accomplished in a setup consisting of a reactor capable of a pressure of about 60 bar, a jacket for heat transfer, and data control and acquisition systems. The detail of the used apparatus is shown in Fig. 1. This apparatus is consisting of a vertical stainless steel tube (1) with an approximate height about of 15 cm, as the nucleation site of crystals. The surface of the tube can be cooled to about -30 ℃ by chilling cycle via R12 refrigerant (2).

This tube is plunged inside a jacketed stainless steel tank (5) filled with 2000 cm^3 of solution (4). The temperatures of T$_0$ and T$_1$ are measured by PT100 thermometers calibrated with maximum uncertainty ±0.1 ℃. The processes of ice freezing and hydrate formation take place on the wall of the vertical tube (1) in the zone (3), and the residual solution (unfrozen phase) is vacated from the drain valve (7). A digital microscope camera (DigiMicro) (9) can be utilized in front of the view window (8) to film the growing ice (or hydrate) layer. Also, a conductivity meter (Aqualytic/AL20Con) was used with the uncertainty of ±0.1 μS/cm to measure the electrical conductivity of brine solution in the initial state and after the solidification process. Moreover, Fig. 2 shows the real pictures of different sections of the experimental reactor.

Experimental Procedure
In this work, the desalination process was studied based on the crystallization method in two sections including the ice solidification and the gas hydrate formation. These processes are based on a phase change of liquid to solid. This phase change occurs *via* temperature variation by a physical process.
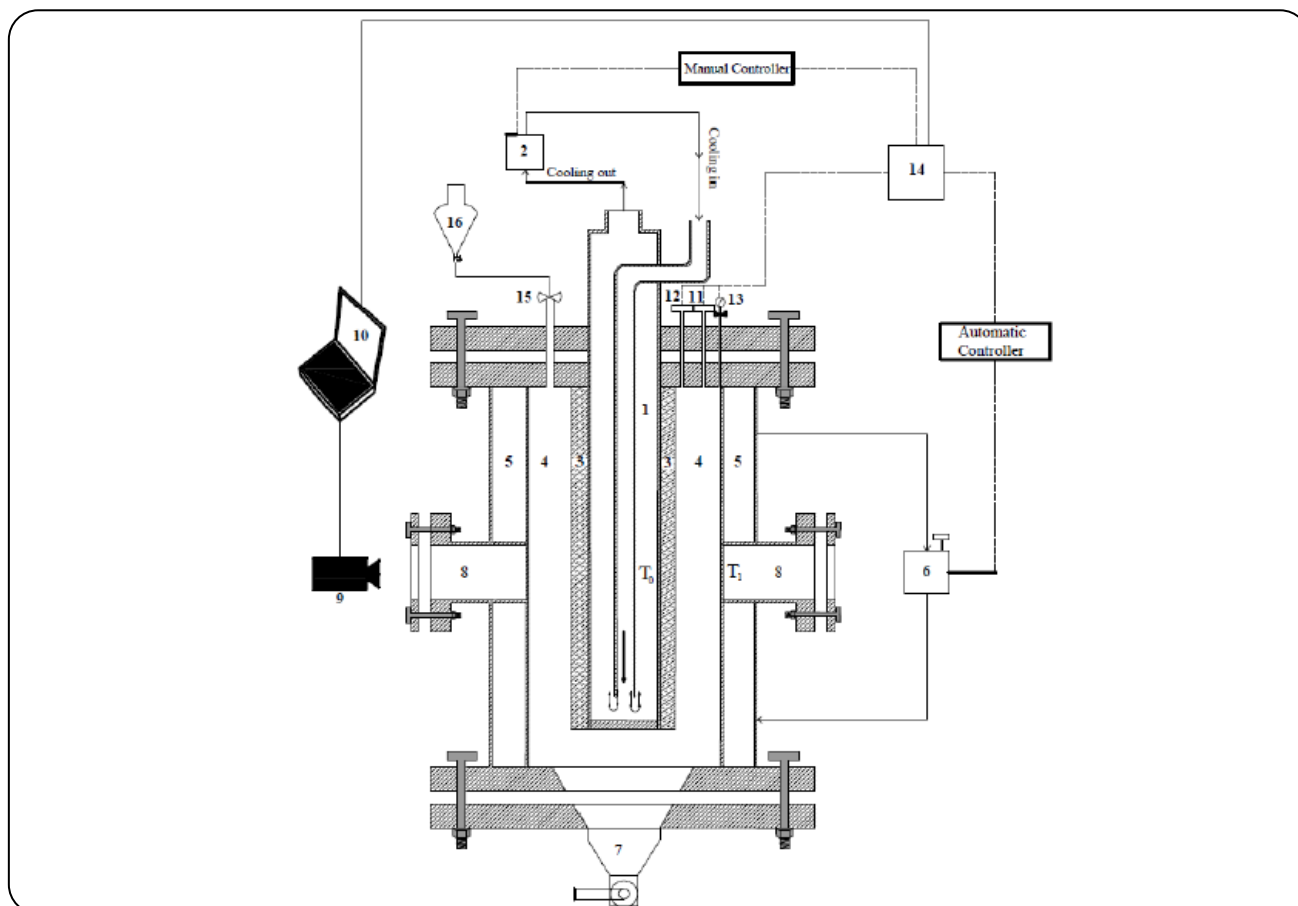
Fig. 1: The experimental setup. 1) Cylindrical refrigerant pipe, 2) chilling cycle via R12 refrigerant (internal chilling),
3) hydrate formation zone, 4) Test solution, 5) double-glazed chamber or thermal jacket, 6) thermostatic bath (external chilling),
7) drain valve, 8) view window, 9) Digital microscope camera, 10) Computer, 11) Thermocouple 1, 12) Thermocouple 2,
13) Manometer, 14) Viewer and data control system, 15) Solution inlet valve, 16) primary brine solution inlet
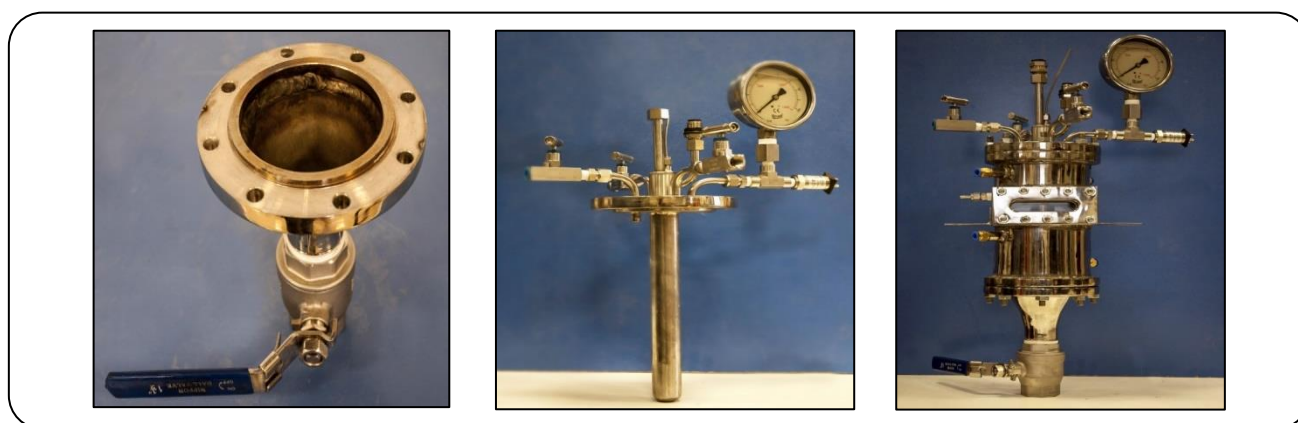

Fig. 2: The real pictures of different sections of the experimental setup.

The freezing point of water is 0.0 ℃ while the equilibrium temperature of THF hydrate formation is about 4.4 ℃. The temperature of the cooled tube (cylindrical refrigerant pipe in Fig. 1 must be adjusted less than the freezing and hydration points. Hence the temperatures -11.5 ℃ for the freezing method and 2.0 ℃ for the THF hydrate formation were considered as the cooling surface temperature to provide the required driving force in

solidification process. So, the operating conditions in freezing experiments are the following: the initial temperature of the solution: 10 °C, cooled surface temperature (T_0): -11.5 °C, and the temperature of the liquid phase (T_1): 6.5 °C. Also, these conditions in hydration experiments are the following: the initial temperature of the solution: 5 °C, cooled surface temperature (T_0): -2 °C, and the temperature of the liquid phase (T_1): 5.5 °C.

Firstly, the initial brine solutions were prepared with a volume of 1500 cm^3 and then injected into the stainless steel tank. The electrical conductivity of solutions was recorded at a temperature of 25 °C. In experiments on THF hydrate formation, the initial brine solution had been mixed with the hydrate former (THF) at the molar ratio of 17:1 and then introduced into the tank. Because of the low temperature of the cooled internal tube, the freezing step led to the formation of an ice (or hydrate) layer on the external surface of the heat transfer tube (tube 1). During this time, the rate of hydrate growth on the tube would be decreased and after solidification and stabilization in the layer thickness, the drain valve was opened to evacuate the residual brine solution. After exiting of brine, the temperature of the heat transfer tube would be suddenly increased and then the crystals held on the surface of the tube were separated from the surface and gained. Then the solutions of purified water, produced by the exact melting of crystals at the temperature about of 70 °C (for purpose of the exact removal of THF in hydrate crystals), were analyzed by Conductivity-metric to determine the concentrations of remaining ions in water.

In this research, the effect of parameters including initial salinity (concentration of salt), salt kind, and type of solidification process were studied on the desalination efficiency. Hence the experiments were performed in the presence of NaCl with concentrations: 0.03, 0.29, 1.80, 10.00, 19.00 and 30.00 kg/m^3; NaBr with concentrations: 0.10, 0.25, 0.51, 1.00, 3.00 and 8.00 kg/m^3; NaF with concentrations: 0.03, 0.05, 0.42, 0.94 and 1.26 kg/m^3; and NaI with concentrations: 0.02, 0.05, 0.75, 0.10, 1.26, 2.50 and 4.50 kg/m^3. The removal efficiency of each salt was determined by measuring the initial and final electrical conductivity of the solution and applying Eq. (1) as mentioned in reference [31].

$$Removal\ efficiency = \qquad (1)$$

$$= \frac{Initial\ Concentration - Final\ Concentration}{Initial\ Concentration} \times 100$$

RESULTS AND DISCUSSION

Firstly, a number of experiments were performed to find the appropriate time for the crystal growth of ice and THF hydrate on the cooled surface in freezing and hydrate methods. Hence the photos of crystals were prepared by the microscope camera per minute. For example, the images of ice and THF hydrate growing crystal were presented in Figs. (3.a) and (3.b) for time intervals of 15 minutes and 60 minutes in the freezing and hydrate methods respectively. The recorded images show that the crystal's growth reaches a steady state after about 1.5 hours in the freezing process and about 5 hours in THF hydrate formation.

The generated results were presented in Tables 2 to 5 for both methods of freezing and hydrate formation. Also, the removal efficiency versus initial salinity was plotted in Figs. 4 to 7 for mentioned salts. The results show the effect of initial salinity on the removal efficiency for different salts. In all brine solutions, the increase of initial concentration causes a decrease in desalination efficiency. Generally, in higher concentrations, the presence probability of salts and impurities rising in crystal lattice; hence the purity of produced crystals can be increased by rising desalination stages.

The type of solidification process, including ice freezing and hydrate formation, can impress the removal efficiency of salts. The plotted curves in Figs. 4 to 7 show that the removal efficiency based on hydrate formation is higher than the removal efficiency in the freezing method for all of the studied ions. Moreover, the temperature of the cooled surface is about -2.0 °C in THF hydrate formation while this temperature is -11.5 °C in the freezing process. So the water desalination process based on hydrate formation requires lower cooling energy to provide the required driving force besides the higher efficiency.

Besides, the influence of hydrate in the freezing method occurs in high concentrations of salt. The related results were given in Table 6 for salts of NaF, NaCl, NaBr, and NaI. For example, for NaBr salt, the removal efficiency of hydrate method is about 1.86 times higher in efficiency than freezing method in concentration of 3 kg/m^3 while the removal efficiency of two methods is similar in low concentrations (0.1 kg/m^3).

Table 2: Desalination results in different concentrations of NaCl.

Experiment method	Concentration (kg/m³)	Initial EC[1] (μS/cm)	Final EC[1] (μS/cm)	Removal Efficiency (%)
	0.03	79.90	43.80	45
	0.29	587.00	286.00	51
Freezing method	1.80	3520.00	2040.00	42
	10.00	17760.00	9850.00	44
	19.00	33100.00	20900.00	37
	30.00	49600.00	35100.00	29
	0.03	79.90	33.70	58
	0.29	587.00	129.00	78
Hydrate method	1.80	3520.00	1145.00	67
	10.00	17760.00	6210.00	65
	19.00	33100.00	14250.00	57
	30.00	49600.00	24400.00	51

1: Electrical Conductivity at 25 ºC

(3.a)

(3.b)
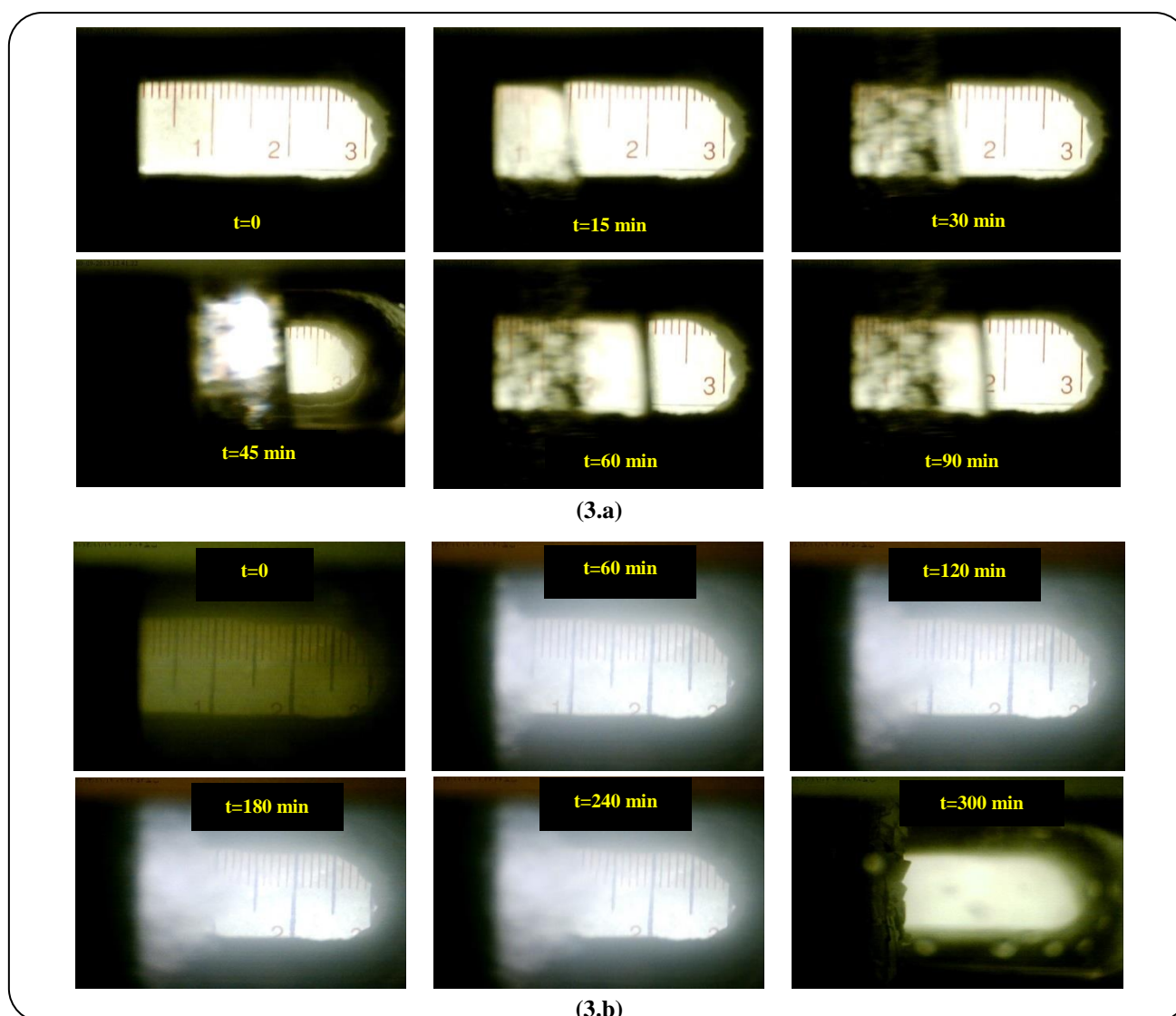
Fig. 3: the images of the growing crystal during crystallization processes; a) ice crystal, b) THF hydrate crystal.

Table 3: Desalination results in different concentrations of NaBr.

Experiment method	Concentration (kg/m3)	Initial EC[1] (µS/cm)	Final EC[1] (µS/cm)	Removal Efficiency (%)
Freezing method	0.10	126.20	38.80	69
	0.25	305.00	79.60	74
	0.51	593.00	177.30	70
	1.00	1161.00	474.00	59
	3.00	3380.00	1921.00	43
	8.00	8870.00	4980.00	44
Hydrate method	0.1	126.20	38.10	70
	0.25	305.00	54.10	82
	0.51	593.00	72.50	88
	1.00	1161.00	162.80	86
	3.00	3380.00	682.00	80
	8.00	8870.00	1618.00	82

1: Electrical Conductivity at 25 ºC

Table 4: Desalination results in different concentrations of NaF.

Experiment method	Concentration (kg/m3)	Initial EC[1] (µS/cm)	Final EC[1] (µS/cm)	Removal Efficiency (%)
Freezing method	0.03	79.10	34.10	57
	0.05	128.60	63.90	50
	0.42	952.00	577.00	39
	0.94	2080.00	1620.00	22
	1.26	2750.00	2080.00	24
Hydrate method	0.03	79.10	54.80	31
	0.05	128.60	64.30	50
	0.42	952.00	567.00	40
	0.94	2080.00	1164.00	44
	1.26	2750.00	1554.00	43

1: Electrical Conductivity at 25 ºC

Table 5: Desalination results in different concentrations of NaI.

Experiment method	Concentration (kg/m3)	Initial EC[1] (µS/cm)	Final EC[1] (µS/cm)	Removal Efficiency (%)
Freezing method	0.025	25.80	9.20	64
	0.05	47.80	18.60	61
	0.10	88.60	37.20	58
	0.75	595.00	226.10	62
	1.26	985.00	394.00	60
	2.50	1931.00	830.30	57
	4.50	3460.00	1903	45
Hydrate method	0.025	25.80	11.20	56
	0.05	47.80	16.80	65
	0.10	88.60	21.10	76
	0.75	595.00	66.80	89
	1.26	985.00	148.20	85
	2.50	1931.00	338.00	82
	4.50	3460.00	419.00	88

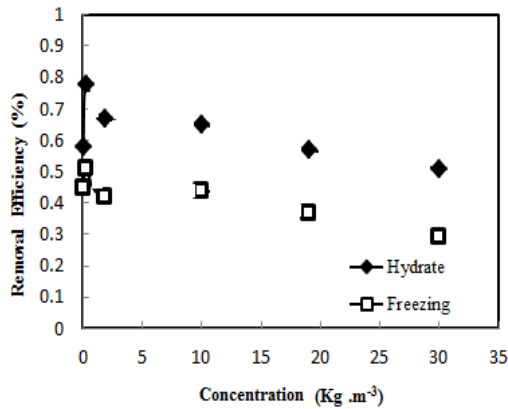*1: Electrical Conductivity at 25 ºC*

Research Article

Fig. 4: Water desalination efficiency in presence of NaCl.
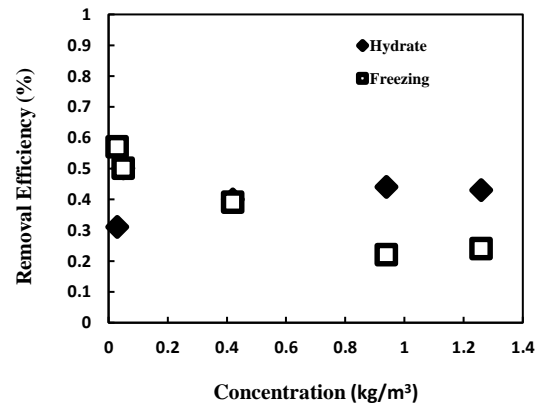

Fig. 6: water desalination efficiency in presence of NaF.
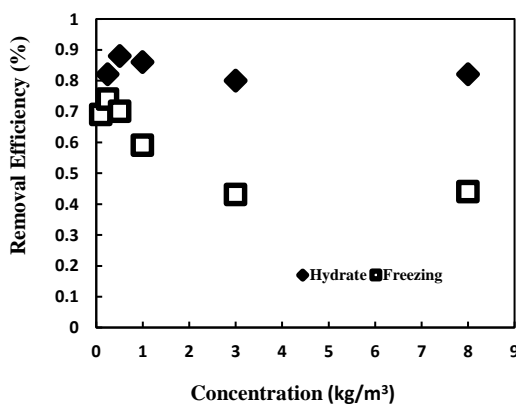

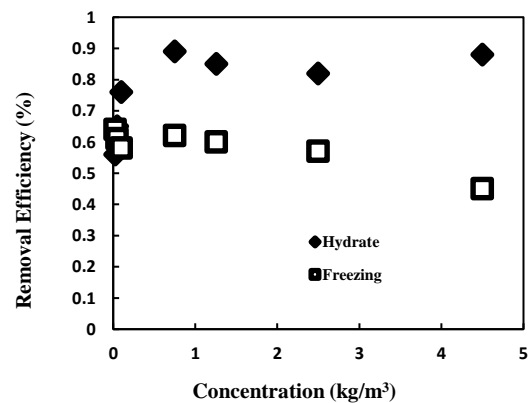*Fig. 5: Water desalination efficiency in presence of NaBr.*

Fig. 7: Water desalination efficiency in presence of NaI.

It seems, in the seldom concentrations the hydration process is similar to the freezing process; so the removal efficiency of the two methods is nearly equal. In low concentrations, the salts perform as the nucleation sites and hence they accelerate the crystal formation process. So the kinetics of crystal growth increases and the removal efficiency of salt is further. With considerable addition in concentrations, the salts perform as the inhibitor and disarrange the crystal lattice structure due to the electrostatic forces between water molecules and ions. These electrostatic forces are stronger than the hydrogen bonds of water molecules therefore it causes the rupture of crystallization structure, the reduction of formation kinetic, and thereupon the decrease of removal efficiency of salts.

Moreover, a number of experiments were performed at two same concentrations (5 mol/m^3) and (30 mol/m^3) of mentioned salts to study the effect of ionic radius.

The ionic radius of F$^-$, Cl$^-$, Br$^-$, I$^-$ ions are 119, 167, 182, and 206 pm respectively. In brine solution with a concentration of 5 mol/m^3, the content of NaF, NaCl, NaBr and NaI salts are 0.21, 0.29, 0.51 and 0.75 kg/m3 respectively. Also in concentration of 30 mo/.m^3, the content of NaF, NaCl, NaBr and NaI salts are 1.26, 1.80, 3.00 and 4.50 kg/m^3 respectively. According to the results, the removal efficiency depends on the ionic size as the salts with higher ionic sizes improve the desalination efficiency. The presence probability of ions with a higher radius in the crystal lattice is less; the larger ions issues easily from the ice or hydrate crystals. So the dissolved mineral components are removed in the following order: I$^-$ >Br$^-$ >Cl$^-$ >F$^-$. Also Figs. 8 and 9 show the removal efficiency versus the ion radius in two concentrations for freezing and hydration methods respectively. The later results are confirmed by the results presented by *Park et al.* which were based on water desalination by CO$_2$ hydrate formation [5].

Table 6: Increase the ratio of the efficiency of hydrate into the freezing method in NaCl, NaBr, NaI, and NaF.

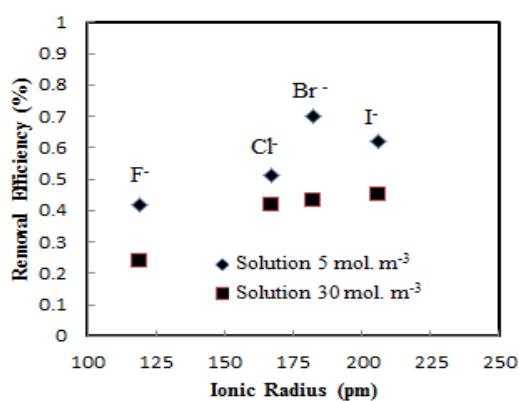| Type of salt	Concentration (kg/m3)	Increase Ratio of Efficiency
	0.03	1.28
	0.29	1.53
	1.80	1.59
NaCl	10.00	1.48
	19.00	1.54
	30.00	1.76
	0.10	1.01
	0.25	1.1
	0.51	1.25
NaBr	1.00	1.45
	3.00	1.86
	8.00	1.86
	0.025	0.87
	0.05	1.06
	0.10	1.23
NaI	0.75	1.30
	1.26	1.29
	2.50	1.30
	4.50	1.49
	0.03	0.54
	0.05	1
NaF	0.42	1.02
	0.94	2
	1.26	1.79

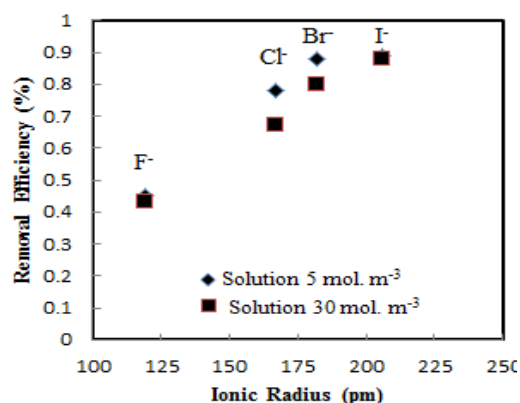*Fig. 8: Water desalination efficiency versus the ion radius in the freezing method.*

Fig. 9: Water desalination efficiency versus the ion radius in THF hydration method.

However, we conclude the following results based on the methods which were used for the experiences:

1) The removal efficiency of salts depends on the ionic size. The removal of salts of higher size is further by the hydrate-based and freezing desalination. The presence probability of ions with a higher radius in the crystal lattice is less; the larger ions issues easily from the ice or hydrate crystals.

2) The efficiency of desalination by hydrate formation is higher than freezing desalination in similar conditions. In the freezing method, the salt removal efficiency is reduced with an increase in salt concentration while different behavior is observed in the hydration process. As in the low concentrations, the removal efficiency of the hydration process is low; and in the higher concentrations, the salt removal is increasing.

3) In low concentrations, the salts perform as the nucleation sites and hence they accelerate the crystal formation process. So the kinetics of crystal growth increases and the removal efficiency of salt is further.

CONCLUSIONS

This paper investigated the solidification step in a static layer crystallizer for salt removal from brine solutions based on the crystallization method including ice freezing and THF hydrate formation processes. The different parameters influencing the desalination process were studied by means of electrical conductivity analyses on the purified water. The brine solutions were supplied in the presence of NaCl with concentrations: 0.03, 0.29, 1.80, 10.00, 19.00, and 30.00 kg/m^3; NaBr with concentrations: 0.10, 0.25, 0.51, 1.00, 3.00 and 8.00 kg/m^3; NaF with concentrations: 0.03, 0.05, 0.42, 0.94 and 1.26 kg/m^3; and NaI with concentrations: 0.02, 0.05, 0.75, 0.10, 1.26, 2.50 and 4.50 kg/m^3. According to the obtained results of the experiences; the removal efficiency of salts depends on the ionic size. The removal of salts of the higher size is further by hydrate-based and freezing desalination. Also, the efficiency of desalination by hydrate formation is higher than freezing desalination in similar conditions.

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