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Experimental Investigation on Freeze-Concentration Process Desalting for Highly Saline Brines

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Abstract**—**Using the freeze-melting process for the disposing of high saline brines was the aim of the paper by confirming the performance estimation of the treatment system. A laboratory bench scale freezing technique test unit was designed, constructed, and tested at Doha Research Plant (DRP) in Kuwait. The principal unit operations that have been considered for the laboratory study are: ice crystallization, separation, washing, and melting. The applied process is characterized as "the secondary-refrigerant indirect freezing", which is utilizing normal freezing concept. The high saline brine was used as definite feed water, i.e. average TDS of 250,000 ppm. Kuwait desalination plants were carried out in the experimental study to measure the performance of the proposed treatment system. Experimental analysis shows that the freeze-melting process is capable of dropping the TDS of the feed water from 249,482 ppm to 56,880 ppm of the freeze-melting process in the two-phase's course, whereas overall recovery results of the salt passage and salt rejection are 31.11%, 19.05%, and 80.95%, correspondingly. Therefore, the freeze-melting process is encouraging for the proposed application, as it shows on the results, which approves the process capability of reducing a major amount of the dissolved salts of the high saline brine with reasonable sensible recovery. This process might be reasonable with other brine disposal processes.

Keywords**—**High saline brine, freeze-melting process, ice crystallization, brine disposal process.

I. INTRODUCTION

THE water pollution from the industrial plants has a serious impact on the environment and it is obviously related to the disposal method of the waste stream that has been produced from the plants. The major challenge associated with the desalination and related industrial plants are the safe disposal of byproduct as high saline brine without harming the environment or public health. Freezing– melting is considered as one of the prominent technique to treat the high saline brine solutions. Further, freezing– melting is classified into direct contact freezing, vacuum freezing, indirect contact freezing, and eutectic separation based on the technique used for the brine treatment [1]. The main sources of high saline brine disposal are water desalination plants, electrical power generation plants, and oil and gas industries where the total dissolved solids (TDS) of brine may reach up to maximum of 100,00 ppm. It is notable that the high saline brines cannot be desalted by using the predictable desalination processes, as known due to two crucial factors which are cost and reliability. Moreover, these factors have limited the scope of choice of other desalination processes for such applications.

This paper presents a solution that can be used to treat brine with minimal harm to the environment using the freezing–melting process. When seawater or other saline waters freeze, the individual ice crystals consist of pure water, thus leaving behind the dissolved organic and inorganic solids (e.g., salt) in liquid pockets of a high-salinity brine. For more details on the freeze-melting process, readers can explore this technique in further detail through the listed references [2]. From an industrial separations viewpoint, technically and economically, the freeze-melting process has many advantages over other conventional desalination processes for treating the extremely high saline water; especially, less energy requirement, and less scaling, fouling and corrosion problems. Furthermore, the capital cost is low because many inexpensive materials (i.e. plastic) can be used, and also, it requires low chemicals due to absence of pretreatment system. Moreover, this process (i.e. freezing) is least harmful to the environment [3]. Yet, there are more or less mechanical difficulties with ice management [4].

A trial research laboratory study was conducted at the DRP in Kuwait existing to confirm the performance of the freeze-melting process for advancing and considering the high saline brine (with rang TDS of 250,000 ppm), to proper level that can be recycled and improved for the same industrial application. Nevertheless, the possibility of techno-economy is away from the scope of this paper.

II. METHODS

A complete bench-scale testing of the freezing technique has been designed, fabricated, constructed, and tested at the DRP in Kuwait as shown in Figs. 1-3 to verify the performance evaluation of the treatment system (i.e. freeze-melting process) for treating the high saline industrial brine. In general, the rig consists of two freezing stages known as "first and second freezing stages", whereas a refrigeration system (i.e. freezer) is employed to freeze the great saline brine solution (which is kept inside the container of each freezing stage as shown in Fig. 1) at low temperatures (-20 °C). The practical process in this trial study is categorized as "secondary-refrigerant indirect freezing" and it uses the normal freezing theory.

The principal unit operations that have been considered in each of freezing stage are ice crystallization, washing, separation, and melting. Therefore, the components of each freezing stage are identical; however, the only difference is correlated to the concentration of feed water that has been used, since the product water from the first stage becomes feed water to the second stage (i.e. successive stages). The materials of the components of each freezing stage have been

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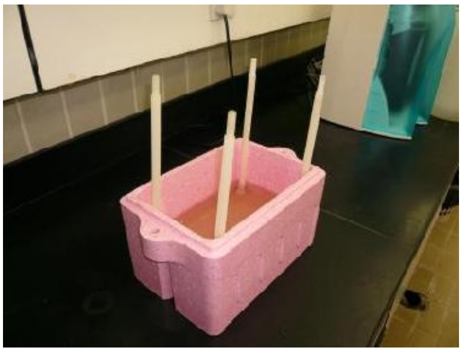
selected based on their ability to resist the reactive and corrosive chemicals during process operation. Furthermore, this material selection is furthermore aimed at escaping the chemical contact between the materials and the brine. It is significant to state that the container of each freezing stage was designed with polystyrene material, and the reason is to insulate (from heat transfer by atmosphere) the surrounding plane walls of the freezing chamber except the top surface, in order to keep the heat removal focused only from the top surface of the brine during crystallization process, hence a thin layer of ice crystals can be produced on the surface brine. This can be separated later by an ice crystallization separator as displayed in Fig. 2.

(a)



(b)

Fig. 1 Freezing stage, freezing chamber, and ice crystallization separator

As definite earlier, four main unit procedures considered in each freezing stage, and they activate with the crystallization process. Each freezing unit is filled with 4 liters of the high saline brine and then the ice crystallization separator is inserted inside the freezing chamber as shown in Fig 1, which fits to the bottom to keep it away from surface of brine, and then the freezing stage itself is kept inside the freezer for nucleation, growth, and crystallization purposes. As shown in Fig 2, the layer of ice crystals must be formed on the surface of the brine, and it can be separated afterwards manually by rising the ice crystallization separator (which has a net barrier) that carry only the ice crystals while the brine can be rejected. It is stated [5] that the brine adhering to the thin plates of ice, and perhaps being retained in the interstices by capillary forces, is responsible for the relatively high salt concentration found in the melted ice (i.e. product). Therefore, the mass of ice crystals (i.e. product) is required to be small (i.e. slushy) rather than a hard solid to drain much of the trapped brine from the mass of ice, and to wash out most of the remainder with fresh water. Hence the mass of ice crystals must be removed from freezer at appropriate time (i.e. monitoring the operation period and the size of ice crystals) during the operation in the freezing process, and also, the produced thin layer of ice crystals must be washed and rinsed to remove (or to minimize) any remaining salts adhering to the ice crystals (i.e. product).

(a)

(b)

Fig. 2 Separation method of ice crystals in the laboratory bench scale testing

Regarding the washing process, the ice must be washed because it crystallizes as a fine slush still stock a considerable quantity of brine in the spaces between the crystals. It is stated [6] that half of the weight of the slush is brine and half is ice. As a result, the core objective of this procedure is to take out the entrained salts from ice crystals (i.e. product) by washing. This process (i.e. washing) can be achieved physically by transferring the produced ice crystals to the container (which has a mesh inside) as shown in Fig. 3. Then, the produced ice crystals are washed by spraying wash water (through a wash bottle). Following this process, the washed ice crystals can be separated by raising the mesh, so the wash water falls in the bottom of the container.

Fig. 3 washing method using a container and mesh

Many considerations have been taken in the washing process, which include: firstly, the concentrations of the washing-waters of the first and second freezing stages are unlike, meanwhile wash water is engendered as of around 5% of the full quantity of the melted clean ice crystals. Secondly, it is important to assure that no wash water is retained in the ice crystals. Thirdly, the wash water must be utilized in washing process at low temperature to avoid melting the ice crystals due to the temperature difference between the wash water and the ice crystals. Following the washing process, the washed ice crystals are then moved to the laboratory beaker and then melted via hot plate to create the final product water of the freezing stage.

III. Results & Discussion

The great saline brine samples of one of the industrial plants in Kuwait were collected, analyzed, and tested in this experiment. It is important to mention that the exact source of the brine is not mentioned due to reasons of privacy. However, the chemical analysis such as the major ionic composition of the high saline brine is indicated in Table I, and also, it is compared with the Arabian Gulf seawater in this paper. Table I shows that the TDS of high saline brine is extremely high with an average TDS of 250,000 ppm and it contains more than 90% of monovalent (Cl^-, Na^+) ions; however, the percentage of hardness ions (i.e. Ca^{+2}, Mg^{+2}, $(SO_4)^{-2}$) is about 8.7%. In comparison with Arabian Gulf seawater, it is revealed that the high saline brine is more concentrated (about five times) than Arabian Gulf seawater.

The first and second freezing stage grades are illustrated in Figs. 4 and 5. These figures show that the first freezing stage was capable of reducing the TDS of feed water from 249,482 ppm to 128,760 ppm with a salt rejection of 56.88%, and a recovery percentage of 44.44%. With respect to the second stage freezing, Fig. 4 displays that the TDS of feed water (which is produced from the first freezing stage) is reduced from 128,760 ppm to 56,880 ppm, while the results of the recovery and salt rejection are 70% and 70.31%, respectively, as shown in Fig. 5. Therefore, it is exposed that the bench-scale testing of the freezing technique was capable of rejecting 80.95% of dissolved salts in the high saline brine (with a recovery ratio of 31.11%), which means that this treatment system decreases the TDS of feed water from 249,482 ppm to 56,880 as shown in Fig. 4.

TABLE I

COMPARISON OF MAJOR COMPONENTS OF ARABIAN GULF SEAWATER AND HIGH SALINE BRINE SAMPLES

Parameter	Units	Arabian Gulf Seawater	Arabian Gulf Beach-well Seawater	Highly Saline Brine
		Ionic Composition	Ionic Composition	Ionic Composition
pH	-	8.40	7.50	6.48
EC	mS/cm	70.6	65.5	229
Ca^{2+}	mg/l	550.0	960.0	18320.0
Mg^{2+}	mg/l	1578.0	1506.0	3134.7
(SO4)2-	mg/l	3841	3600	350
$(HCO_3)^-$	mg/l as $CaCO_3$	128.0	158.6	155.5
Cl^-	mg/l	22277	25600	146000
Na^+	mg/l	13170	16608	94717
TDS	mg/l	46110	46348	250664

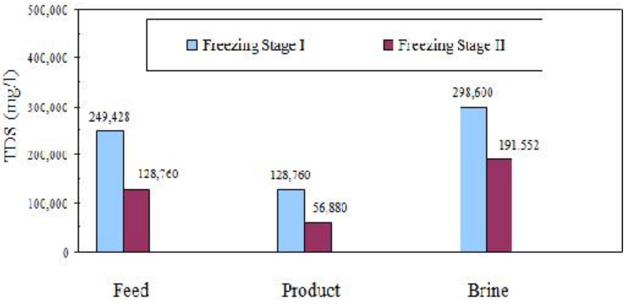


Fig. 4 First and second freezing stages feed, product, and brine

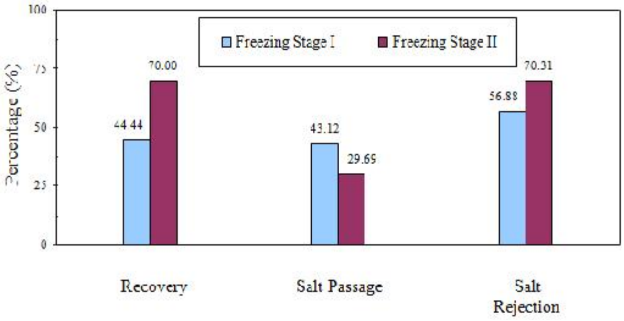


Fig. 5 First and second freezing stages recovery, salt passage, and salt rejection

Fig. 6 shows a basic schematic diagram of the presentation of the structure which contains a summary of the TDS outcomes for the first and second freezing stages. With respect to wash water, the volume of wash water (which was used up for washing procedure for two freezing stages) is 5% of the product water. Fig. 6 explains that the Arabian Gulf beach-well seawater was used for washing the ice crystals in the first freezing stage, while the distilled water was used as a wash water in the second freezing stage. Next, the TDS of the wash water was improved from 46,348 ppm to 224,308 ppm in the first freezing stage, and increased radically from 1 ppm to 110,405 ppm in the second freezing stage as shown in Fig. 6.

It is observable that the wash water was capable of taking away important volume of salts from the ice crystals in the two freezing stages.

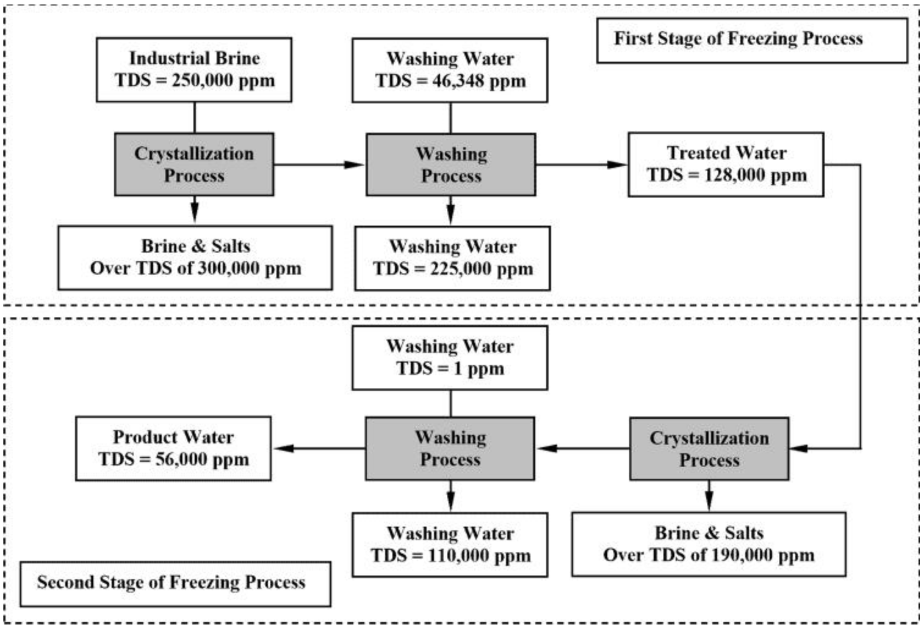


Fig. 6 Simplified block diagram of the process description and performance of the two stages of bench-scale testing using the freezing technique

IV. CONCLUSIONS

The significant results from this paper display that the freeze-melting process has numerous advantages over the other desalination technologies for sanitizing the high saline brine, particularly, in energy condition, fouling, scaling, and corrosion. Achievement of 75–90% by freezing desalination could reduce energy in the compulsory for the conventional thermal process [7].

Due to the capital low cost, several low-cost materials (i.e. plastic) can be used, and also it needs low chemicals due to lack of pre-treatment system, It also has the benefit of a low operational temperature, which reduces corrosion and scaling complications [8]. Therefore, low-cost plastics or cheap materials can be used at low temperature [9]. Freezing desalination process does not require pre-treatment stage, hence chemical products for pre-treatment are avoided. Also, it does not cause to fouling, comparable to membrane desalination. [10]. Also, it is harmless for the environment.

The experimental results on the performance of the treatment system (i.e. freeze-desalting process) were promising and showed that this procedure is exactly adept to decrease an important quantity of the melted salts from the high saline brine with reasonable recovery. On the other hand, the quality of the ice is affected by some issues through the freezing desalination process [11]. The results show that this treatment system might be competitive with the other brine disposal processes.

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