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The analysis of salt production by a recrystallization method using the concentrated backflow effluent of the desalination units

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ABSTRACT

Considering the fact that many oil-rich regions are located on the coastlines and islands, desalination units need to be established in these regions in order to supply required fresh water. In desalination units, a stream of concentrated saline water is also produced in addition to fresh water. This concentrated saline water is returned to the sea and may cause severe environmental problems in the region. Applying proper operations on the output-concentrated saline water from the desalination units not only prevents the salinity shock, as well as the thermal shock to the marine ecosystem, but it could produce two valuable products of fresh water and refined salt. In this study, first, the output-concentrated saline water from a desalination unit in Pars Special Economic Energy Zone, situated in south of Iran, is chemically treated to decrease the level of calcium and magnesium. Then, this purified concentrated saline water is concentrated in an electrodialysis machine to increase the salt level to about 20%. Then, the output concentrated solution is directed from electrodialysis into a crystallizer, in which it is heated to reach a saturated or supersaturated concentration, in order to form salt crystals. The slurry of the produced salt crystals and saline water is directed from the crystallizer to a centrifuge in order to separate salt crystals from the saline water. The separated salt crystals are dried and then analyzed. The analysis reveals that a high-quality salt is produced by this method.

Keywords: Fresh water; Salt; Desalination units; Salinity shock; Heat shock; Recrystallization

1. Introduction

The earth is home to about 1.4 billion m^3 water of which only about 2.5% (35,000,000 m^3) is potable water [1]. The lack of sufficient potable water in the World has prompted man to find and increase the production of water with a desirable quality (potable water) in the last few decades. On the other hand, statistics reveal that the demand for water has been doubled in every 15 years in the World during the last 50 years [2]. Therefore, the number of water desalination units, that turn the saline water into fresh potable water using different methods, has been increasingly improved in many countries all over the World.

In water desalination units, a stream of concentrated saline water is usually produced that might cause severe environmental problems in the region [3].

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Aquatic creatures can live in a certain temperature and salinity of water. If they are exposed to heat or salinity shocks, they will not be able to tolerate such shocks and will be harmed [3]. Most microorganisms living in the sea can bear a salinity change (salinity shock) of 1,000 mg/L. Considering the fact that the sea water is directed to the water desalination units, such as reverse osmosis (RO) units [4], with a salinity level of 35,000 mg/L, and the saline water is returned to the sea in a concentration of about 70,000 mg/L, then this output saline water has to be diluted with the sea water about 35 times in order to protect and preserve microorganisms [5]. Such a dilution process will demand a large running cost and cost of capital. On the other hand, when we consider the compound of the output concentrated saline water produced from these units, we will observe that the solution of such concentrated saline water mostly constitutes NaCl (or salt). Other materials constitute only a limited percentage of such compounds. Therefore, the application of an appropriate operation on the output saline water driven from desalination units will yield two valuable products of refined salt as well as fresh water.

The comparison between desalination units and the salt production units using a recrystallization method reveals that there are shared parts in these units, and the output-concentrated saline water driven from the desalination machine will provide a desirable input for feeding the recrystallized salt production unit. Indeed, using the output saline water from the desalination machine, as the input for the salt production unit that utilizes a recrystallization method, will have the following environmental and economical advantages:

(1) The salinity and heat shock will be avoided at the discharge point of concentrated saline water into the sea, and the aquatic creatures will not die and the regional ecologic system will not be harmed.
(2) Salt will be produced with a desirable quality in a considerable quantity.
(3) A greater amount of fresh water will be produced.
(4) The establishment of salt production units at the vicinity of desalination units will result in employment.

Several studies have been done in this field and numerous articles have been published. Turek [6] examined the dual purpose of water desalination using electrodialysis (ED) technique and salt production from its output. Considering the production of both salt and water, he obtained the estimated cost of 30$ per ton of salt and 0/44$ m^{-3} of water, and so he recommended this process very valuable and profitable. Tanaka [7] had examined a method for the simultaneous production of salt and fresh water from seawater by reverse osmosis (RO) and ED methods. Davis [5] had introduced the zero discharge desalination technique that produces fresh water, salt and other valuable substances simultaneously.

2. Qualitative and quantitative analysis of concentrated saline water flown back to the sea from different desalination units

In order to analyze the environmental issues resulted from returning the concentrated saline water into the sea, as well as the significance of producing salt out of this stream, it is of great significance to qualitatively and quantitatively analyze the concentrated saline water returned from different desalination units into the sea. Such an analysis reveals the volume of saline water that is returned to the sea every day and the degree of quality of this water, and the potentials this saline water might possess for production of salt or other valuable solutes.

2.1. Quantitative analysis

Pars Special Economic Energy Zone [8] is currently equipped with two desalination units of reverse osmosis type. The capacity of the produced fresh water, the saline water that is returned to the sea, as well as the level of existing salt in each one of the backflows from these units are illustrated in Table 1.

2.2. Qualitative analysis

The input fed to different desalination units is the Persian Gulf water. The properties of input fed, as well as the properties of the backflow from two studied units are illustrated in Table 2.

Table 1
The capacity of different desalination units in Pars Special Economic Energy Zone (August 2009)

Unit	Produced fresh water (m^3/day)	Concentrated saline water backflow (m^3/day)	The amount of salt existing in the concentrated saline water backflow (kg/day)
Noor Vijeh	10,000	6,666	389,961
Hyundai	5,000	3,333	175,482
Total	15,000	10,000	565,443

Table 2
Properties of Persian Gulf water and the backflow stream from two studied units (August 2009)

Stream characteristics	Input stream (Persian Gulf water)	Backflow from Noor Vijeh unit	Backflow from Hyundai unit
Concentration of sodium chloride (mg/L)	32,994	58,500	52,650
Concentration of sulphate (mg/L)	2,640	5,280	38,400
Electrical conductivity (μs/cm)	49,397	72,250	63,493
TDS (mg/L)	43,708	67,970	57,115
pH	8.08	7.55	7.70
Total alkalinity (mEq/L)	155	205	200
Total hardness (mg/L)	7,250	12,000	10,000
Calcium concentration (mg/L)	600	1,250	950
Magnesium concentration (mg/L)	1,380	2,130	1,830

3. The process of refined crystallized salt production from concentrated saline water backflow

Desalination units are important considering both their production rate and the concentration of salt in their effluents. So, extraction of salt from these effluents not only prevents the introduction of salinity shock at its diffusion point into the sea, but also helps in the production of a considerable amount of salt with a high degree of purity. In this study, the optimal method for the production process of salt from the concentrated saline water diffused from desalination units is investigated. In order to produce salt from the diffused concentrated saline water, the following operation should be applied to the concentrated saline water:

(1) Purification of the output concentrated saline water from impurities.
(2) Concentration of the purified saline water to an supersaturation level and production of salt crystals.
(3) Separation of salt crystals from the slurry of salt and saline water.
(4) Drying of the produced salt crystals.

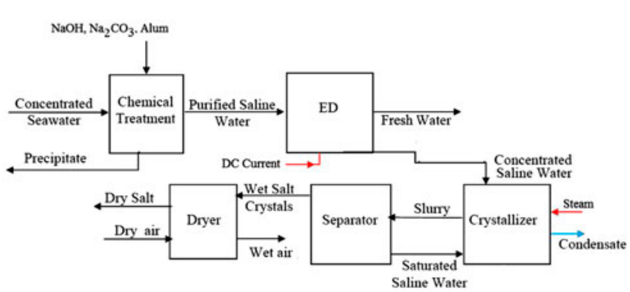

Fig. 1. Block diagram for salt production process from the concentrated saline water outflow.

Each of these operations, and the construction of the required machine needed for this operation are discussed below. The block diagram for salt production process from the concentrated saline water outflow is illustrated in Fig. 1.

3.1. *Chemical purification unit for the concentrated saline water outflow from the impurities*

In addition to NaCl, there are other ions, such as Mg^{++} and Ca^{++}, in the seawater. These impurities reduce the purity of produced salt from desalination effluent and so should be removed. Substances such as sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) are used to remove these ions by formation of $CaCO_3$ and $Mg(OH)_2$ deposits. To accelerate the deposition process, aluminum sulfate ($Al_2(SO_4)_3$) is used as coagulant. Coagulants form larger particles and make deposition process easier.

In this study, a purification unit including two tanks equipped with stirrers with variable speed is used in order to remove the impurities. The first tank is equipped with rapid mixing rate stirrer for the reactions to be performed, and the second tank is equipped with slow mixing rate stirrer in order to form the lumps and remove them out of the space. To add additives such as sodium hydroxide and sodium carbonate to the first tank, a controllable and measurable valve is used so that it will be possible to obtain the optimal amount for the needed substances, as well as the stirrer rate and the desirable retention time, using different experiments.

In these experiments, the effects of parameters such as pH of the solution, the amount of added sodium hydroxide, sodium carbonate and aluminum sulfate, and also the weight percentage of each of them, temperature of the operation, retention time and the stirrers' speed are examined and the optimal condition for the removal of the maximum undesirable material from the system and preparing the highest purity of saline water is specified. In these experiments, after purification of the solution, the water is completely evaporated and the purity degree of the salt is achieved. The general scheme of the chemical purification unit is illustrated in Fig. 2.

3.2. Purified saline water concentrating unit

Electrodialysis (ED) uses the electricity power to move the ions existing in the solution through the membrane [9]. In this study, an ED unit is used for concentrating the purified saline water. Although by using ED unit in the salt production process, we meant to increase the NaCl concentration in the solution and decrease the heating load of the crystallizer; in this study, the electrodialysis also increases the purity of the concentrated saline water. This is done by selectivity property of the membrane for different ions. The ED unit used in this study increases the concentration of the salt in the input saline water up to 20%. The schematic diagram of the laboratory ED unit is illustrated in Fig. 3.

3.3. Salt crystals production unit (crystallizer)

Crystallization is the process by which a chemical is separated from a solution as a high-purity, definitively shaped solid.

To produce salt crystals with a high-purity degree, a crystallizer was designed and constructed. This machine is a draft tube baffle crystallizer [10]. In this study, the aim is to design and specify the thickness and different dimensions of a crystallizer, in order to produce 5 kg of salt per hour from the saline water with the salt concentration of 20%. Considering the salt concentration of 20% for the input solution, 20 kg water per hour should be evaporated in order to produce 5 kg salt per hour. The heat exchanger used in the crystallizer to supply the needed energy is a shell-and-tube heat exchanger, in which steam is passed through the shell and the saline water stream passes through the pipe.

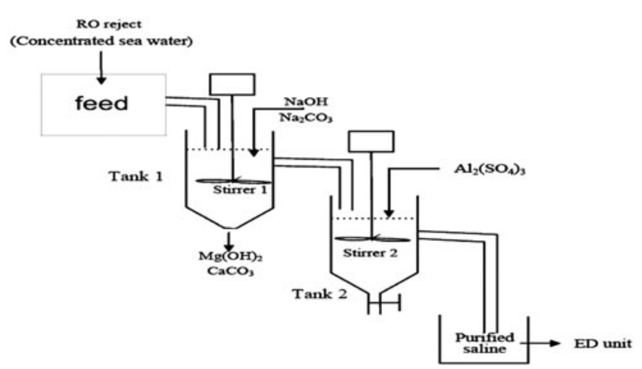

Fig. 2. Schematic diagram of the saline water purification unit.

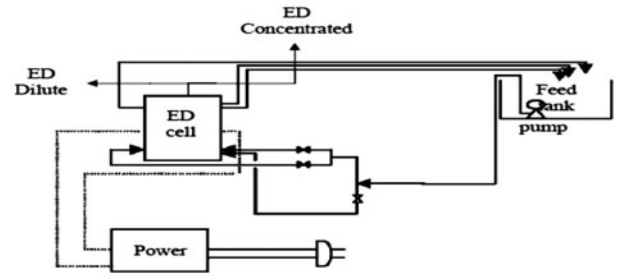

Fig. 3. Schematic diagram of the laboratory ED unit.

3.4. Separator of salt crystals from salt and saline water slurry

Centrifugation is a separation process, which uses the action of centrifugal force to promote accelerated settling of particles in a solid–liquid mixture.

In this study, the output from the evaporator which is a two-phase solution of liquid slurry and solid salt crystals is entered into a laboratory-scale centrifuge. This unit performs the separating operation of water and salt as two phases [11]. The centrifuge used in these experiments is a rotating centrifuge with four test-tubes.

3.5. Drying of the produced salt crystals

Drying is a mass transfer process consisting of the removal of water or another solvent by evaporation from a solid, semi-solid, or liquid [12]. Different types of dryers could be used for this purpose. In this study, a tunnel dryer was designed and constructed. The solid salt, as the output of the centrifuge, is quite wet. So, it is poured into the dryer to remove the moisture. A fan is set at the opening of the dryer, the revolution of which can be adjusted. The air flow is produced by this fan and is passed through some electrical elements inside the dryer. The warm and dry air flows over the wet salt crystals and dries the salt crystals.

4. Analysis of the dried salt crystals

These processes properly work only if the salt is produced based on national and international standards. The edible salt is subject to obligatory standards. The first standard for salt in Iran was

Table 3
Properties of the salt produced by recrystallization method in bench scale

Property	Value	Measuring method
Total hardness	50 mg/L	E.D.T.A standard titration
Hardness of calcium	14 mg/L	E.D.T.A standard titration
Hardness of magnesium	35 mg/L	(Total hardness)—(hardness of calcium)
Sulphate percentage	0.2%	E.D.T.A standard titration (0.01 mol/L)
Purity	99.6%	Mohr's method of titration

codified by Institute of Standard and Industrial Research of Iran (ISIRI). This standard has been revised for three times. The third revision was implemented in April 2006. The minimum level of purity of salt in this standard is 99.2% [13].

Salt should enjoy the following specifications to be considered as acceptable: physical properties such as shape, taste, smell, dross, and size of crystals; chemical properties including purity, insoluble material in the water, solved sulfate in water, humidity, and level of iodine. The properties for a sample of salt produced by the above-mentioned process and their measuring method are illustrated in Table 3. The comparison of these properties with the standard table for salt of Iran reveals that all features meet the final National Standard of Iran.

5. Design of various units

The design of various units is done according to backflow stream parameters from NoorVijeh desalination unit. The target is to design a salt production plant with a production capacity of 3 ton/h.

5.1. Design of chemical purification unit

The properties of backflow stream from the NoorVijeh desalination unit is given in Table 2. Other parameters that are obtained experimentally and could be used for design reactors and storage tanks are shown in Table 4.

Based on these data, and residence time and mass balances equations, the volumes of the reactors and storage tanks are calculated. The required volumes of the reactor I and reactor II are 5.625 and 6.75 m^3, respectively. The volume of storage tanks for caustic soda is 7.29 m^3 and for soda ash is 1.62 m^3.

5.2. Design of purified saline water concentrating unit (electrodialysis)

In order to increase the concentration of purified saline water, a bench-scale ED unit was designed and built. The ED unit includes a feed tank which stores salty water, a pump ($p = 0.27$ kw), a membrane unit which consists of cationic and anionic ion exchange membranes, and a rectifier that provides power with different voltages. Each membrane has an effective area of $60 \times 65\,mm^2$. Translocation of the membranes inside the ED unit is shown in Fig. 4.

According to Fig. 4, the distance between the membranes in dilute sections is 4 mm and the same in concentrated section is 3 mm. Electric potential is supplied by the electrodes. Both electrodes are made of pure platinum with a $2.4 \times 2.4\,mm^2$. Using Faraday equation for the current of electrodialysis [16], the

Table 4
Input data for design of the salt production unit

Property	Value
Incoming flow of saltwater (m^3/h)	45
The amount of alum used (cc/L)	0.5
The amount of caustic soda used (cc/L)	4.5
The amount of sodium carbonate used (cc/L)	0.5
The concentration of used caustic soda	25%
The concentration of used soda ash	25%
The concentration of used alum	10%
Agitator speed in the first reactor (rpm)	2,500
Agitator speed in the second reactor (rpm)	500
Hydraulic retention time in the first reactor (HRT1), min	5
Hydraulic retention time in the second reactor (HRT2), min	6

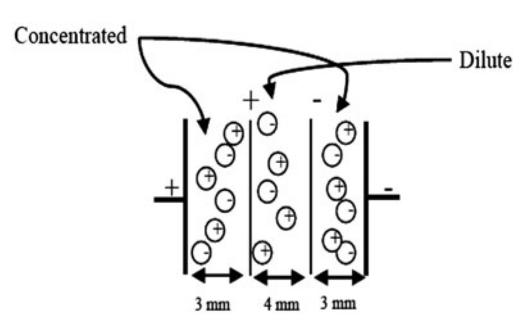

Fig. 4. Translocation of the membranes inside the ED unit.

required electric power is approximately 20 MW assuming 6 V potential of DC current and using 500 cells.

$$I = \frac{F \times \mathrm{N} \times Q \times E_1}{n \times E_2}$$

where F is Faraday constant (96,487 C/g-eq.), N is normality of feed (g-eq./L), Q is flow rate (L/s), n is quantity of cells, $E1$ and $E2$ are electrodialysis and current efficiency.

Table 5
Specifications and parameters needed for the design of forced circulation crystallizer

Parameter	Value
Production rate, P_c (t/h)	3
Medium production size, L_M (μm)	0–300
Coefficient of variation for the product C_V (%)	20–25
Feed concentration, C_f, (kg/kg)	0.20
Specific heat of feed, C_{pf} (kJ/kg K)	3.29
Density of feed, ρ_f (kg/m^3)	1,185
Feed temperature, T_f (°C)	20
Evaporator entry temperature, T (°C)	55
Boiling point elevation, e (°C)	7
Additional undercooling, ΔT (°C)	2
Vapor condensation temperature, T_v (°C)	46
Vapor pressure, P_v (kN/m^2)	10
Vapor density, ρ_v (kg/m^3)	68.7×10^{-3}
Latent heat of vaporization, λ (kJ/kg)	2,400
Steam saturation temperature, T_s (°C)	66
Product slurry concentration, M_{TP} (kg/m^3)	250
Density of crystals, ρ_c (kg/m^3)	2,115
Dynamic viscosity of slurry, μ_{sl} (Ns/m^2)	$23 \times 10^{-}4$
Specific heat of solid crystals, C_{ps} (kJ/kg K)	0.877
Specific heat of slurry, C_{psl} (kJ/kg K)	2.7
Density of slurry, ρ_{sl} (kg/m^3)	130

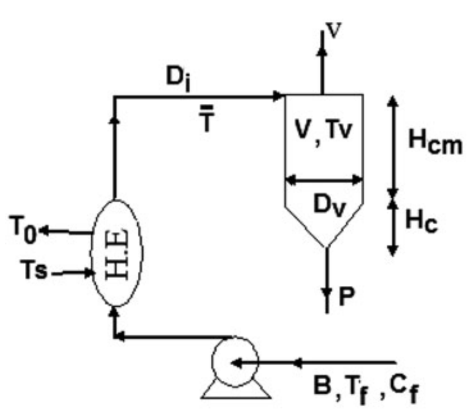

Fig. 5. Schematic view of the forced circulation crystallizer.

5.3. Design of salt crystals production unit (crystallizer)

In this unit, concentrated salt water solution, which approximately contains 20% of salt is evaporated by application of heat and vacuum until supersaturated concentrations are reached. At this concentration, the salt crystal nuclei produced and

Table 6
Calculated design parameters for the required crystallizer

Parameter	Value
Product flow rate, P (t/h)	15.6
Vapor flow rate, V (t/h)	3
Feed flow rate, B (t/h)	30.6
Salt production flow rate, P_C (t/h)	3.0
Required input energy, q_i (kW)	10,979
Flow of solution, Q (m^3/h)	2815.1
Diameter of the cylinder, D_V (m)	3.28
Input rate to crystallizer, v_i (m/s)	2.7
Inlet pipe diameter of crystallizer, D_i (m)	0.4
Outlet pipe diameter of crystallizer, D_o (m)	0.27
Equivalent pressure head of pump, h (m)	0.85
Minimum height of the cylinder, H_{cm} (M)	4.0
Min. volume of solution inside the crystallizer, V_1 (m^3)	33
Height of the cone zone, H_c (m)	3.6

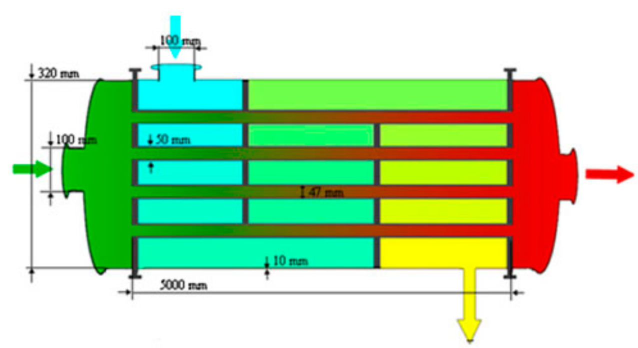

Fig. 6. Schematic and calculated parameters of the required heat exchanger.

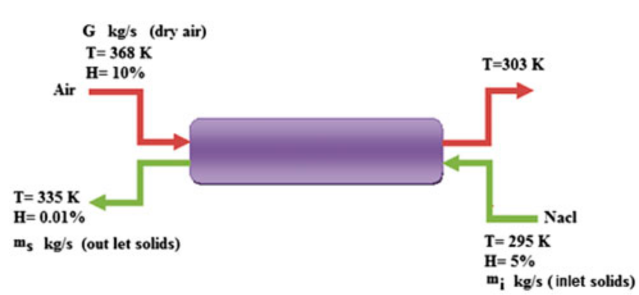

Fig. 7. Schematic view of a nonaligned rotary dryer.

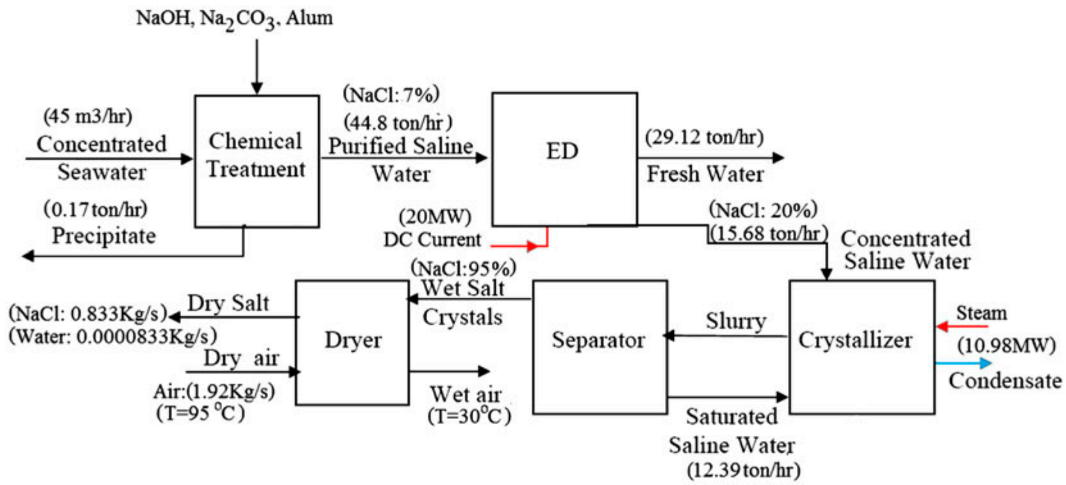

Fig. 8. Brief results of mass and energy balance.

gradually grow to reach the desired size. After the formation of crystals, salt crystals and water slurry from the outside of the unit is sent to a centrifuge unit. In the centrifuge unit, under the influence of centrifugal force, the salt crystals are separated from the water. According to the crystallization of the salt intended to be done, it is recommended to use forced circulation type crystallizer [14–16]. Specifications and parameters needed for the design of forced circulation-type crystallizer are given in Table 5 [17].

According to Fig. 5, where a schematic view of the forced circulation crystallizer is shown [16], the application of material balance equations for salt and water will result in different design parameters for this unit as shown in Table 6.

Using the relevant formulas, required parameters for design of used heat exchanger such as required heat, number of tubes, and distance between them are calculated [16]. Calculated design parameters for the required heat exchanger in the crystallizer are given in Fig. 6.

5.4. Design of rotary dryer

A stream of wet salt with the humidity of 5% and temperature of 295 K is fed to a rotary dryer. The output salt with the moisture content of 0.01% and temperature of 335 K is exit from the other end of the dryer. Heated air is blown counter-currently with the humidity of 10% and temperature of 368 K into the rotary dryer and comes out with the temperature of 303 K. To produce 3,000 kg of dry salt per hour, rotary dryer should receive approximately 3,150 kg of wet salt per hour.

According to Fig 7, below relations can be found in the principle of mass conservation for the solid salt as shown in Fig 7.

Considering governing mass and energy balance for the dryer, the mass flow of wet solid is 3,150 kg/h of which 150 kg/h is amount of water and 3,000 kg/h is dry salt, and the required air flow rate of dryer is 1.92 kg/s. The diameter and length of the dryer are 1.6 and 8 m, too.

6. Brief of mass and energy balance

The mass and energy flow rates of different streams which were approached in the previous section are shown in Fig. 8. The required energy of the salt dryer is obvious as a supplied hot air flow.

7. Conclusion

In this work, the possibility of establishing a recrystallized salt production unit using the effluent of seawater desalination units was studied. The obtained results showed that this process not only could prevent damaging of sea ecosystem by salinity and thermal shocking, but also produces high-quality food-grade salt and fresh water. The proposed salt unit receiving 45 m^3/h of concentrated brine can produce 0.833 kg/h salt and 29.12 ton/h treated water with consumption of 10.9 MW steam energy.

Acknowledgment

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