Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20927

79 (2017) 93–102
June

Treatment of sulphate wastewater by freeze desalination

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Received 30 July 2016; Accepted 11 May 2017

ABSTRACT

Cooling and freezing can be used to produce fresh water from brackish water, industrial brines and leachates from industrial wastes. The aim of this study was to identify how cooling and/or freezing can be used for the recovery of drinking water from sulphate rich solutions associated with various cations. It was found that: (i) If the solution contains only Na_2SO_4, after pre-treatment with sodium alkalis, it can be removed from solution through cooling down to 0.33 mol/L (31.7 g/L SO_4) through crystallization of $Na_2SO_4 \cdot 10H_2O$; (ii) the solubility of Na_2SO_4 upon cooling is influenced by the Cl-concentration; (iii) the Reverse Osmosis-Cooling (ROC) process is most suitable for treatment of saline solutions rich in Na_2SO_4, as it can be precipitated through cooling as $Na_2SO_4 \cdot 10H_2O$, followed by reverse osmosis to produce drinking water; (iv) The energy required to cool water, containing 100 g/L Na_2SO_4, from 25°C to 0°C, amounts to 10.66 kWh/t water. When the water is further cooled down to freeze 90% of the water, the energy consumption increased from 10.66 kW/h to 37.74 kWh/t.

Keywords: Freeze desalination; Reverse osmosis cooling

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1. Introduction

The potential of freeze desalination of sea water to produce drinking water was derived from the natural phenomenon of pure ice formation from frozen sea water [1,2]. This led to the realization of the possibility of using freezing to produce fresh water from brackish water, industrial brines and leachate from industrial wastes [3–5].

The major benefit of freeze desalination over current brine treatment technologies, e.g. distillation and evaporation, derives from the much lower heat of fusion of ice (333 kJ/kg) compared to the heat of evaporation of water (2500 kJ/kg). The theoretical energy required to drive an evaporation process is seven times more than that of a freezing process. Although this does not take into account the possibility of energy recovery in both systems, the potential economic benefits of using freeze desalination remain high. Progressive and suspension freeze crystallization can be used. Progressive freeze crystallisation (PFC) is a method based on a single ice crystal formed on the cooling plate. This method enables easy-handling of ice because of its one-dimensional operation. PFC has the disadvantage that energy utilization is poor due to isolation of the cooling surfaces with an ice layer [6]. In suspension freeze crystallization (SFC), many small ice crystals form and can be obtained by providing a scraper mechanism on the cooling surfaces and a stirrer to distribute the cool energy throughout the total solution. The most prominent freeze desalination (FD) technologies studied in South Africa are the HybridICE® technology [7] and the Eutectic Freeze Crystallization (EFC) process [8]. The former is a freeze concentration process which continuously recovers fresh water as ice without necessarily crystallizing

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Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, Rome, Italy, 22-26May 2016

the dissolved species. The latter is a combination of freeze concentration and freeze crystallization of dissolved solutes. HybridICE® is a suspension, freeze desalination technology that employs scraped surface heat-exchangers to generate ice from wastewaters (e.g. brine), which is then separated from the concentrate by means of a static filter [7,9–12,]. The University of Cape Town has partnered with Delft University of Technology in the development of an EFC process which selectively precipitates dissolved salts, making it possible to produce saleable by-products from brine treatment [13]. Ice contamination by the mother liquor is a drawback of these processes since the ice crystals are grown in the presence of highly concentrated brine. To counteract this, a washing stage is incorporated in the EFC process [13].

The freezing stage can be divided into: (i) A stage where only ice will crystallize and, (ii) a stage where ice and salt will crystallize out. Of importance is to produce a clean ice to ensure good salt recovery and water of a quality that allows it to be reused. Van der Ham et al. [14] observed that rapid nucleation and crystal formation results in impure ice crystals due to fast growth. They overcame this problem by making provision for slow crystal growth in a separate tank with a long residence time. Addition of ice seed crystals also contributes to a better quality ice during batch operations as it suppresses secondary nucleation [15,16]. Crystals with a small particle size are preferred overcrystals with a large particle size to: (i) Provide a larger number of seed crystals that can prevent the formation of new nucleation sites [17] and (ii) allow a rapid rate of crystallization [18]. Seeding should to be applied shortly after the precipitation of ice or salt occurs to avoid spontaneous occurrence, of the metastable limit [16]. Lewis et al. [8] have used a cooling rate of between 1.5°C/h–6°C/h to avoid secondary nucleation.

The Reverse Osmosis/Cooling (ROC) process was developed for scenarios where pre-treatment is required for the removal of all ions that could cause membrane fouling during RO or NFdesalination as shown in Fig. 1 [19]. In the second stage, RO or NF is used to produce clean water and a highly concentrated brine with a TDS >100 g/L. In the third stage, the brine, containing mainly Na_2SO_4, is cooled to allow $Na_2SO_4{\cdot}10H_2O$ crystallization. No freezing is required in the ROC process. Therefore, this study was aimed at (i) Predicting the solubility of various salts, (ii) determining the behaviour of $Na_2SO_4{\cdot}10H_2O$ during cooling through progressive freeze desalination (no scraping of wall surfaces of the beaker) and suspension freeze desalination (regular scraping of wall surfaces of the beaker), (iii) identifying factors that influence the rate of ice crystallization and ice purity for solutions where the salt concentration is below its solubility and (iv) identifying the most cost-effective solution from an energy perspective.

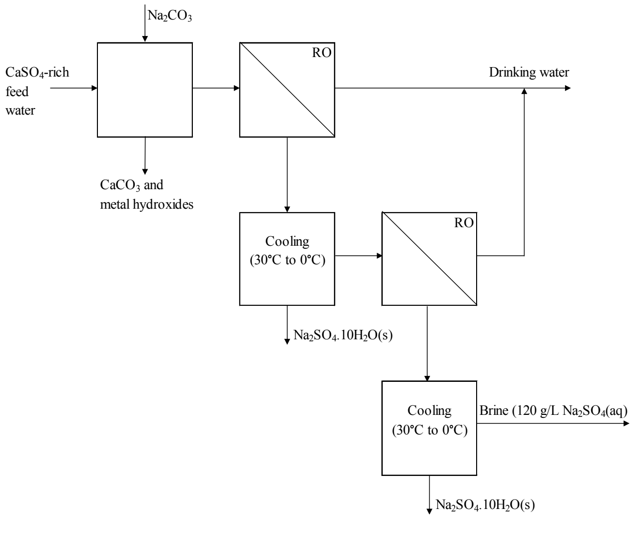

Fig. 1. Schematic flow-diagram of the ROC process

2. Materials and methods

2.1. Feedstock

Tap water was used for the preparation of synthetic feed brine from NaCl(s), and $Na_2SO_4(s)$ salts (Sun Salt Services [Pty] Ltd) as presented in Table 1.

2.2. Batch experiment set-up

Batch experiments carried out in beakers were performed to study the behaviour of dissolved Na_2SO_4, NaCl and $MgSO_4$ solutions during cooling. The cooling process was always started at ambient laboratory temperature down to the freezing point, which was another variable depending on the brine composition and levels of salt ion species. Beakers containing the solutions were positioned in the cooling bath that was cooled approximately to temperatures around –10°C depending on total salt ion concentration. Ethylene glycol was used as a primary refrigerant in the cooling bath. In the case of Na_2SO_4 crystallization, Na_2SO_4 seed crystals were added at 10°C to serve as seed for the salt crystallization. The cooling had an effect of lowering the solubility of Na_2SO_4. Early formation of ice caused rapid concentration of the salt in the mother liquor. In the case of $MgSO_4$ studies, ice crystals were added at –1°C to promote ice crystallization. Temperature, conductivity, sulphate, magnesium, sodium concentrations and mass of ice and solid $Na_2SO_4{\cdot}10H_2O$ were measured over time.

2.3. Experimental procedure

The effects of the following parameters on the temperature and rate of crystallization of $Na_2SO_4{\cdot}10H_2O$ were determined during batch experiments viz:(i) Na_2SO_4 concentration (0, 4, 25, 50, 100, 200 g/L) (ii) NaCl concentration

Table 1
Chemical composition of simulated brine from a reverse osmosis plant that treats sulphate rich mine water

Parameters	Simulated RO Brine
Sodium, mg/L	35,840
Chloride, mg/L	5,900
Sulphate, mg/L as SO_4	66,900
TDS, mg/L	108,571
Cation, meq/L	1,600
Anion, meq/L	1,600

(0, 10 and 50 g/L); (iii) $MgSO_4$ concentration (220 g/L); and (iv) Ice seed crystal dosing rate (0, 10, 30 g/250 mL).

2.4. Analytical procedure

The composition of the synthetic feed-brines and the crystallized products were determined by using appropriate analytical techniques. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine sodium, magnesium and sulphate, while the chloride was determined using the titrimetric method and conductimetric method was used to measure electrical conductivity. The temperature was measured using a calibrated Knick Stratos Eco 2505 rapid temperature measuring meter. The ice content was determined by mixing 250 mL ice slurry (mass m_1; temperature T_1) with 200 mL (m_2) warm water (T_2). The mass of ice (m_i) was determined calorimetrically by determining m_1 (mass of cold water and ice), T_1 (temperature of cold water and ice), m_2 (mass of hot water), T_2 (temperature of hot water), and T_3 (temperature of mixture after ice has melted). An excel add on software called Goal Seek on MS Excel software was used to calculate mass of ice (m_i) using the following equation:

$$4.18\,(m_1 - m_i)\,(T_1 - T_3) + 330\,m_i + 4.18\,m_2(T_2 - T_3) = 0 \qquad (1)$$

3. Results and discussion

Freeze crystallization deals with three types of processes namely: (i) Salt crystallization from saline solutions such as that of Na_2SO_4(aq) before freezing point is reached; (ii) Ice crystallization when salts concentrations in solution are below their saturation level at the freezing point and (iii) when ice and salt crystallize simultaneously (eutectic point).

3.1. Solubility of Na_2SO_4

One of the main unwanted components from RO is highly concentrated brine rich in Na_2SO_4(aq). Solid salts of sodium sulphate exists in three forms namely anhydrous Na_2SO_4(s), heptahydrate, $Na_2SO_4{\cdot}7H_2O$(s) and decahydrate, $Na_2SO_4{\cdot}10H_2O$ [20]. The solubility of each of the three sodium sulphate salts decreases with temperature and $Na_2SO_4.10H_2O$(s) start to crystallise out of solution at temperatures < 30°C and the mother liquor brine will be approximately 30 wt% of sodium sulphate. Fig. 2 shows the binary phase diagram of Na_2SO_4–Water system [21]. The diagram shows the regions of stability for various hydrates of sodium sulphate as a function of Na_2SO_4(aq)) concentration and mixture temperature. The transition point, where the stable crystalline form of sodium sulphate changes from Na_2SO_4(s) to $Na_2SO_4{\cdot}10H_2O$(s) is at approximately at 33.13 mass % Na_2SO_4(aq) and the mixture temperature of 32.27°C. For this investigation, the focus was on the lower temperature region where $Na_2SO_4{\cdot}10H_2O$(s) is the dominant crystalline form of Na_2SO_4(aq).

The effect of cooling on the removal of various ions from the brine in the form of crystalline salts is shown in Table 2 and Fig. 3 as predicted by the *OLI* modelling software. From the modelling data, it was observed that the solubility of $Na_2SO_4$was greater than 300,000 mg/L at 25°C and just about 43,494 mg/L at 0°C. This characteristic behaviour of Na_2SO_4 was used in the ROC process for the desalination of brine streams from RO treatment process. The results generated by the *OLI* software were within the range of data obtained during laboratory studies (Table 3) where Na_2SO_4 rich water was cooled. By cooling, sulphate removal from solution was achieved from 63,303 mg/L down to <21566 mg/L at –1°C because of $Na_2SO_4{\cdot}10H_2O$ (Mirabilite) crystallization. The modelling and experimental data on sulphate concentration in solution as a function of temperature was plotted as shown in Fig. 4. The two concentration temperature curves in Fig. 4 had close correlation (0.9899). The removal of sulphate as a crystalline salt of $Na_2SO_4{\cdot}H_2O$(s) resulted with a residual mother liquor brine with 21,566 mg/L SO_4^{2-}(aq) concentration after cooling to –1°C the brine during batch studies. The modelling data with OLI package gave residual sulphate level of 23,514 mg/L in solution after cooling to 0°C. The experimental data and modelling data was within 8% deviation from each other, which is close enough, as deviations of up to 10% are at times acceptable for bulk processes. The preceding values, represent sulphate concentrations of 31.9 g/L (as Na_2SO_4(aq)) and 34.8 g/L respectively. These values were slightly lower than the 42 g/L concentration at the eutectic point. The lower value for sulphate concentration than that expected at the eutectic point was explained by the 5000 to 7000 mg/L chloride in solution. Due to the presence of chloride in solution, the stoichiometric Na^+ concentration was higher than the SO_4^{2-}concentration. This resulted in a lower SO_4^{2-}concentration than predicted for a solution containing no Cl^- ions.

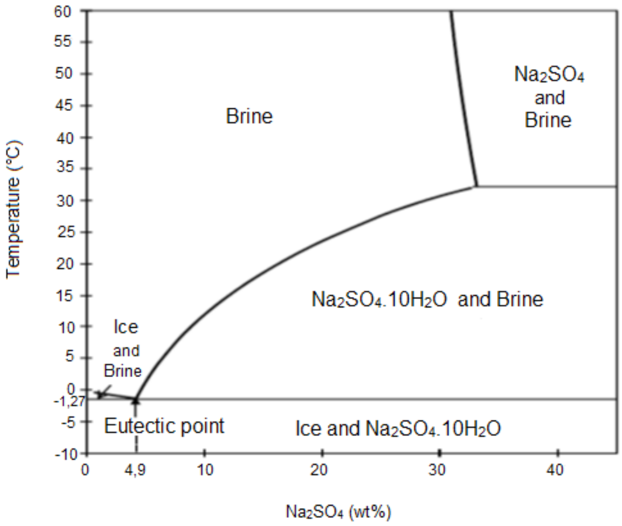

Fig. 2. Binary phase diagram for Na_2SO_4–Water, showing regions of stable phases [21].

In the ROC process, a concentrated brine is produced with a concentration of >100 g/L Na_2SO_4(aq). By cooling from 25°C down to 0°C, $Na_2SO_4{\cdot}10H_2O$ is crystallized out. In the case where water contains only Na_2SO_4, SO_4^{2-} will crystallizes to its eutectic SO_4^{2-} concentration of 28.4 g/L as SO_4^{2-} of $Na_2SO_4{\cdot}10H_2O$(s). With the presence of Cl^- in the water, the SO_4^{2-} concentration in solution, upon cooling, will

Table 2
Effect of temperature on the concentration in solution of Na_2SO_4 (as predicted by *OLI* software)(Feed water composition before cooling (mg/L): Na^+ = 34 815; Ca^{2+} = 69; Mg^{2+} = 69; Cl^- = 5 331; SO_4^{2-} = 65 887; TDS = 106 117)

Temp., °C	Na^+ Aq tot, mg/L	Ca^{2+} Aq tot, mg/L	Mg^{2+} Aq tot, mg/L	Cl^- Aq tot, mg/L	SO_4^{2-} Aq tot, mg/L	TDS, mg/L
25	34,815	69	69	5,331	65,887	106,171
20	34,815	69	69	5,331	65,887	106,171
15	34,815	69	69	5,331	65,887	106,171
10	30,550	69	69	5,331	56,985	93,003
5	20,768	69	69	5,331	36,572	62,809
0	14,511	69	69	5,331	23,514	43,494

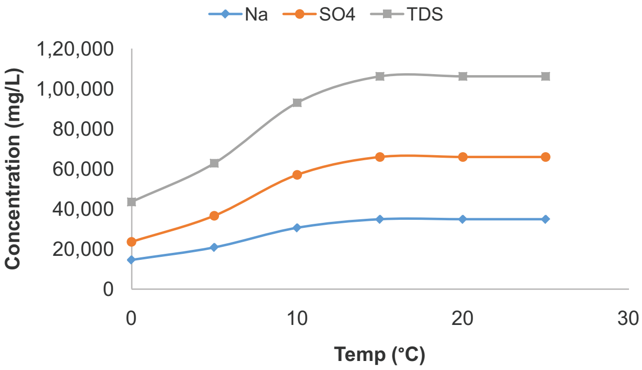

Fig. 3. Effect of temperature on the solubility of Na_2SO_4 as predicted by *OLI* software (Feed water composition before cooling (mg/L): Na^+ = 34 815; Ca^{2+} = 69; Mg^{2+} = 69; Cl^- = 5 331; SO_4^{2-} = 65 887; TDS = 106 117).

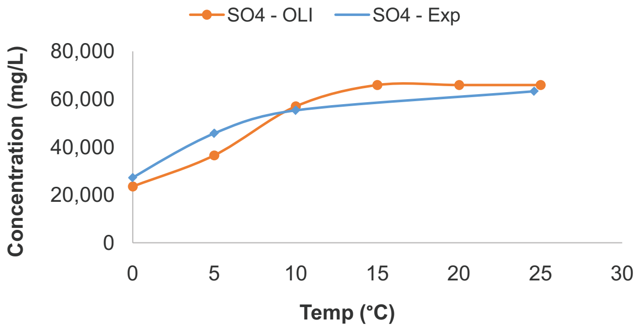

Fig. 4. Comparison between experimental determined and OLI predicted values for SO_4^{2-} concentration in solution as a function of temperature with for a water with initial concentrations of Na^+ = 34 815; Ca^{2+} = 69; Mg^{2+} = 69; Cl^- = 5 331; SO_4^{2-} = 65 887; TDS = 106 117).

Table 3
Removal of Na^+ and SO_4^{2-} as Na_2SO_4 through cooling alone (Water/glycol cooling bath @temperature = –20°C)

Temp, °C	Brine concentration			
	Conductivity, mS/cm	Na^+, mg/L	SO_4^{2-}, mg/L	Cl^-, mg/l
24.6	81.3	30,332	63,303	5,469
10.0	78.2	26,514	55,333	7,219
5.0	64.3	21,896	45,696	6,431
0.0	44.2	13,047	27,229	7,875
–1.0	40.2	10,334	21,566	7,438
–3.0	36.4	8,580	17,907	7,000
–4.1	33.2	7,456	15,561	7,044
–1.4	29.2	8,917	18,609	6,956
–1.5	30.8	8,172	17,055	7,438
–1.3	35.4	8,624	17,998	7,438
–1.4	54.1	8,111	16,927	9,188

decrease due to the higher stoichiometric Na^+concentration compared to SO_4^{2-} concentration values. Freeze crystallization must deal with two scenarios namely: (i) crystallization of ice to the concentration where salts start to crystallize, and (ii) simultaneous crystallization of ice and salt.

3.2. Effect of NaCl on the solubility of Na_2SO_4

Fig. 4 shows that, the higher the NaCl concentration, the lower was the equilibrium SO_4^{2-} concentration, due to $Na_2SO_4{\cdot}10H_2O$ crystallization at temperatures as low as 0°C. At 0°C the solubility decreased from 0.3 mol/L (42.6 g/L) for zero mol/L NaCl to 0.1 mol/L (0.142 g/L) for 10 mol/L NaCl. This was ascribed to the Na^+ that was a common ion to both the salts and the solubility product Ksp = $[Na^{2+}]^2[SO_4^{2-}]$. The graphs (Figs. 3 and 4) were based on an initial Na_2SO_4 concentration of 100 g/L (0.70 mol/L), explaining the maximum values of 0.7 mol/L.

3.3. Crystallizationof $Na_2SO_4{\cdot}10H_2O$ during cooling

3.3.1. Solubility

Zikalala [22] reported that Na_2SO_4 seed crystals increased the rate of $Na_2SO_4{\cdot}10H_2O$ crystallization. This finding needs to be corrected. The lower solubility reported for increased Na_2SO_4-dosages can be explained by the fact that less free water was left in solution as a portion of the water was utilized for the formation of $Na_2SO_4{\cdot}10H_2O$. If the Na_2SO_4 concentration in solution is expressed as a function of the free water left in solution, a constant value was obtained for the solubility of Na_2SO_4.

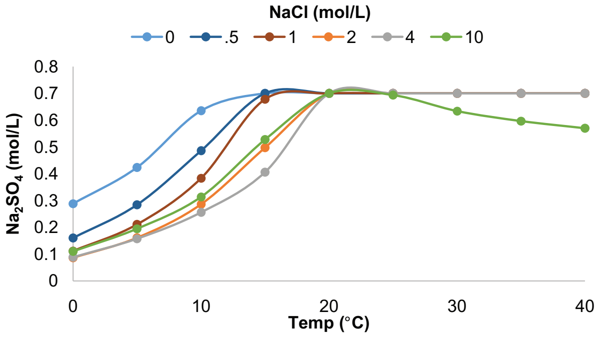

Fig. 5. Effect of NaCl concentration and temperature on the solubility of Na_2SO_4(Initial Na_2SO_4-concentration = 100 g/L).

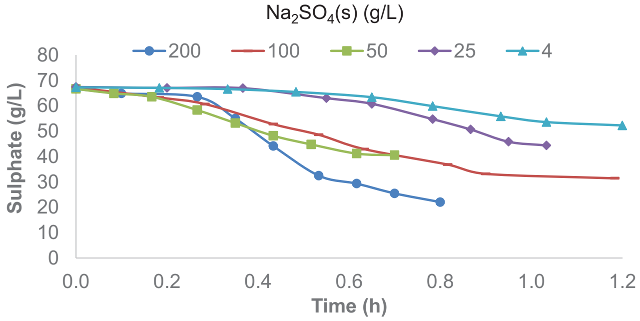

Fig. 6. Effect of excess Na_2SO_4 (in solid form) on the rate of $Na_2SO_4{\cdot}10H_2O$ crystallization (NaCl (aq) = 0 g/L; Na_2SO_{4i} (aq) = 100 g/L; Na_2SO_4(s) = 4, 25, 50, 100 and 200 g/L added in solid form when temp reached 10°C).

3.3.2. Kinetics

Zikalala [22] studied the kinetics of $Na_2SO_4{\cdot}10H_2O$ crystallisation. Fig. 6 shows the results when a 100 g/L Na_2SO_4 solution was first cooled down to 10°C, before pre-cooled Na_2SO_4 seed crystals were added to determine their effect on the rate of $Na_2SO_4{\cdot}10H_2O$ crystallization. The rate of crystallization of Na_2SO_4 was directly related to the mass of Na_2SO_4 seed crystals present. The results showed that the rate of crystallization was influenced by the super-saturation level, the driving force for crystallization. The proposed kinetic equation for $Na_2SO_4{\cdot}10H_2O$ crystallization is given, below :

$$R = k{\cdot}S{\cdot}(C - C_e)^2 \quad (2)$$

where R = reaction rate (mol/ (L/h)); S = Na_2SO_4 seed crystal mass (g/L); C = $Na_2SO_4{\cdot}10H_2O$ concentration in solution (mol/L) and C_e = $Na_2SO_4{\cdot}10H_2O$ concentration at equilibrium (mol/L).

3.4. Factors influencing ice purity from saline solution

Both progressive and suspension freeze crystallization can be used. Progressive freeze-concentration (PFC) is a method whereby a single ice crystal formed on the cooling plate. This method has the disadvantage that energy utilization is poor due to insulation of the cooling surfaces by an ice layer. In suspension freeze crystallization (SFC) many small ice crystals form and can be distributed by providing a scraper mechanism on the cooling surfaces and using a stirrer to distribute the “cold energy” throughout the total solution.

Table 6 shows the effect of various parameters on the rate of ice formation and ice purity for a solution that contained 86.4 g/L $MgSO_4{\cdot}7H_2O$, which is much lower than its solubility (450 g/L at 0°C).Table 6 shows the various parameters which have little effect on ice purity at such a high $MgSO_4{\cdot}7H_2O$ concentration:

- Progressive versus suspension freeze crystallization. By comparing Experiment 1.1–1.3 with Experiment 2.1–2.3 the results showed that the rate of FC was faster with SFC as compared to PFC by comparing the mass of ice that was formed after 0.5; 1.0 and 2.0 h freezing time. This was ascribed to insulation of the cooling surface in the case of PFC. The ice purity was slightly better in the case of PFC.
- Rate of ice crystallization (Experiments 5.1 and 5.2) showed that reducing the rate of ice crystallization from 400 – 160 g ice/ (L·h^{-1}) had little effect on ice purity.
- Ice seed crystal concentration (Experiments 7.1–7.3). A slight improvement in ice purity was obtained with increased ice seed crystal dosages.
- Various compounds behave different during freeze crystallization (Experiment 5.1–5.5). When 30 g/L of NaCl, $CaCl_2$, $MgSO_4{\cdot}7H_2O$ and Na_2SO_4 solutions were frozen to 50% of their volumes, the percentage salt concentration in the ice amounted to respectively 57%, 50%, 54%, 76% and 79% of the salt concentrations in the brines.

Another important parameter to produce clean ice is washing, Chang et al. found that wash water needed to clean ice amounted to 50% of the raw ice where vacuum filtration was used to separate ice from the washing water [23].

4. Energy requirements

4.1. Freeze desalination

4.1.1. Water flow, chemical mass and energy balance model

Energy consumption during cooling and freezing of water containing salt can be calculated thermodynamically. A water flow, chemical mass and energy balance model was developed by Mtombeni et al. [19] incorporating the following stages: Ice crystallizer/cooler; fluidised bed reactor/clarifier for ice/salt separation; ice/brine separator; ice washing stage and feed-brine pre-cooling (latent energy recovery) (Fig. 7, Table 4).

The input parameters for the model were: feed flowrate, target ice-recovery and chemical composition of feed water. The output parameters were: ice produced; brine concentrate and composition; solids concentration in the brine; energy consumption and energy cost. Table 4 shows the calculated values for the various parameters and the formulas that were used.

A typical brine produced from reverse osmosis treatment contains mainly 30 g/L Na_2SO_4. It was calculated that energy utilization amounted 37.74 kWh/m^3 feed and the energy cost to R 26.42/m^3 feed (90% ice yield; R 0.70/kWh). These figures were based on the following assumptions: Feed flow of 10 m^3/h; Na_2SO_4 concentration of 30 g/L; 90% ice yield; COP of 3; electricity price of R 0.70/kWh. Table 5

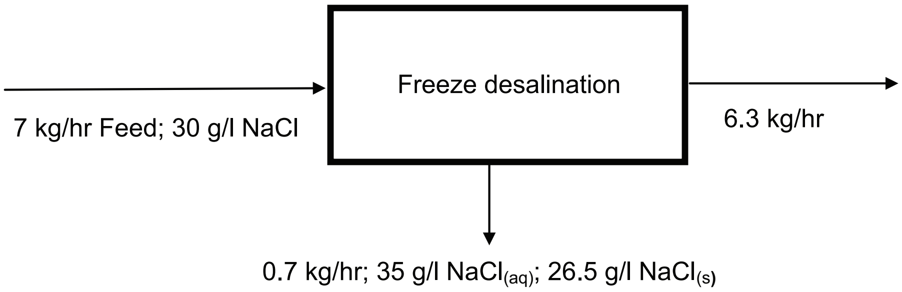

Fig. 7. Simplified configuration of freeze desalination process

Table 4
Water flow, chemical mass and energy balance model [19]

Parameter	Freeze Desalination
Feed	
Feed (m3/h)	10
NaCl (g/kg H2O)	0
Na2SO4 (g/kg H2O)	30
Ice/Brine	
Feed to Freeze (kg/h)	10 000
Ice yield, Y (%)	90.00
Flow ice, m_i (kg/h)	9 000
Residual Brine flow, m_b (kg/h)	1 000
Feed to Freeze/ROC, m_F (t/h)	
NaCl (g/kg brine)	-
Na2SO4 (g/kg brine)	300.00
Flow ice, m_i (g ice/kg feed)	900
Residual Brine flow, m_b (g H2O/kg feed)	100
Solid	
Na_2SO_4 in feed, C_N (g/kg)	30
Na_2SO_4 conc. at freeze point, C_{Nf} (g/kg)	48.17
Na_2SO_4 conc. at freeze point, C_{Nf} (g/l)	47.22
Na_2SO_4 crystallized (g/kg brine)	251.83
Na_2SO_4 crystallized, m_N (kg/h)	251.83
Na_2SO_4 crystals in brine, C_{Ns} (g/kg feed)	25.18
Thermodynamic data	
Specific heat capacity H_2O, C_p (kJ/(kg.deg)	4.2
Specific heat capacity Ice, C_i (kJ/(kg.deg)	2.1
Latent heat of freezing, H_f (kJ/kg)	330.0
Latent heat of fusion: NaCl, H_N (kJ/kg)	430.0
Latent heat of fusion: Na2SO4 (kJ/kg)	196.9
Energy	
Feed temp (deg C)	25
Cold temp (deg C)	0
Energy needed to freezing point, E1 (kJ/h)	1 046 750.0
Energy to freeze brine, E2 (kJ/h)	2 970 000.0
Energy recovered by cooling brine, E3 (kJ/h)	-
Latent heat of NaCl cryst, E4 (kJ/h)	0.0
Latent heat of Na_2SO_4 cryst, E4 (kJ/h)	49 586.1
Energy to salt, E5 (kJ/h)	49 586.1
Total energy needed, E (kJ/h)	4 066 336.11
Energy efficiency, Y_E (%)	99.8
Actual energy required, E_R (kJ/h)	4 076 445.70
Power consumption P_c (kWh/t)	113.23
COP	3.00
Electrical Power (kWh/t feed)	37.74
Electrical Power usage P_u (kWh)	377.45
Cooling Capacity (kW)	1 132.35
Energy cost	
Power price, P_P (R/kWh)	0.70
Power cost, P_C (R/m3)	26.42
Running cost (R/m3)	4.50
CAPEX	
Capacity needed (MW)	1.13
Capex (Euro/MW)	2 000 000
R/Euro	15.00
Capex (R/MW)	30 000 000
Capex Freeze Desalination (R)	33 970 381
Total Capital (R/(Ml/d))	141 543 253
Capital Redemption (20y; 10%/a) (R/m3)	44.93
Chemicals (R/m3)	0.00
Total Running cost (R/m3)	75.85

Table 5
Effect of salt concentration on energy required for (i) cooling and (ii) freezing of water at 25°C

Ice recovery	Solution			Brine feed	Na_2SO_4	NaCl	Initial Temp	Final Temp	dT	Feed		Solids (g/kg feed)		Solids	Energy (kJ/t feed)			Energy (kWh/t feed)	Energy cost (R/m^3 feed
Ice	H_2O	Na_2SO_4	NaCl							Na	SO_4	Ice	Na_2SO_4	Na_2SO_4	Cold Temp	Ice	Na_2SO_4		
%	g/L	g/L	g/L	m3/h	g/kg	g/kg	°C	°C	°C	g/kg	mg/kg	g/kg	g/kg	kg/h					
0	1 000	254.4	314.5	10	100	0	25	25	0	32.4	67.6	0	0.0	0.0	0	0	0	0.00	0.00
0	1 000	132.1	312.6	10	100	0	25	15	10	32.4	67.6	0	0.0	0.0	418 700	0	0	2.36	1.65
0	1 000	66.8	310.7	10	100	0	25	5	20	32.4	67.6	0	31.3	312.9	837 400	0	61 602	6.98	4.88
0	1 000	47.2	309.7	10	100	0	25	0	25	32.4	67.6	0	51.8	518.3	1 046 750	0	102 061	10.66	7.46
5	950	47.2	309.7	10	100	0	25	0	25	32.4	67.6	50	54.2	542.4	1 046 750	165 000	106 803	12.24	8.57
10	900	47.2	309.7	10	100	0	25	0	25	32.4	67.6	100	56.7	566.5	1 046 750	330 000	111 545	13.81	9.67
50	500	47.2	309.7	10	100	0	25	0	25	32.4	67.6	500	75.9	759.2	1 046 750	1 650 000	149 481	26.42	18.49
75	250	47.2	309.7	10	100	0	25	0	25	32.4	67.6	750	88.0	879.6	1 046 750	2 475 000	173 190	34.30	24.01
90	100	47.2	309.7	10	100	0	25	0	25	32.4	67.6	900	95.2	951.8	1 046 750	2 970 000	187 416	39.02	27.32
90	100	47.2	309.7	10	30	0	25	0	25	9.7	20.3	900	25.2	251.8	1 046 750	2 970 000	49 586	37.74	26.42

Table 6
Cost comparison between freeze desalination and the ROC process

Item	Flow (m^3/h)	Na_2SO_4 (g/L)	Energy (kWh/m^3)	Comment
Energy figures:				
Energy requirement of RO (kWh/m^3)			4.00	
Energy requirement of cooling (kWh/m^3)			10.66	
Energy requirement for freezing (kWh/m^3)			26.78	
Freeze desalination				
Feed	1	30		
Cool from 25°C to 0°C	1	30	10.66	
Freeze 90% of the Feed (Melted ice)	0.9	0	26.78	
Brine 1	0.1	300		
Total			37.44	
ROC				
Feed	1	30		
RO permeate	0.7	0	4.00	1 × 4
RO brine (100 g/L Na_2SO_4) (Brine 2)	0.3	100		
Cooling of brine 2	0.3	45	3.20	0.3 × 10.66
Freeze desalination of brine 2	0.3	45	8.03	0.3 × 26.78
Total			15.23	

shows the energy requirement, when brine containing 100 g/L Na_2SO_4 is, (i) Cooled from 25°C to 0°C; and (ii) Frozen to recover from 0% to 90% ice. It was found that upon cooling from 25°C to 0°C, the energy consumption increased from zero to 10.66 kWh/(t brine) while Na_2SO_4 recovered as a solid increased from zero to 518 kg/L Na_2SO_4 brine. When the brine was further cooled to form ice, the energy consumption increased from 10.66 to 37.74 kWh/(t brine) while Na_2SO_4, recovered as a solid, increased from 518 to 952 kg/L Na_2SO_4 brine.

4.1.2. ROC Process

It was shown above that 37.7 kWh/m^3 is needed to convert 90% of brine containing 30 g/L Na_2SO_4 to ice during freeze desalination [24]. Only 10.66 kWh/m^3 was needed for cooling of the brine from 25 to 0°C, and 26.78 kWh/ m^3 (37.74–10.66 kWh/ m^3) for freezing 90% of the water. The energy consumption of 37.7 kWh/m^3 for freeze desalination with a 90% water recovery can be reduced significantly by using the ROC process configuration in the case of brines that contain mainly Na_2SO_4. Table 6 shows the energy requirements when the water containing 30 g/L Na_2SO_4 (Feed) is first concentrated to 100 g/L Na_2SO_4 with RO (brine 2), followed by freeze desalination of brine 2. It was noted that the energy consumption of 37.7 kWh/m^3 for freeze desalination can be reduced to 15.23 kWh/m^3 feed water by including the ROC process. This saving can be increased further by having a next stage of RO/Freeze desalination or by recirculation of brine 2 after cooling to the previous RO stage.

Assumptions:

1. RO energy consumption = 4 kWh/m^3
2. TDS of RO permeate = 0 mg/L
3. TDS of melted ice = 0 mg/L

5. Conclusions

It was found that: (i) If the solution contains only Na_2SO_4, after pre-treatment with sodium alkalis, it can be removed from solution through cooling down to 0.33 mol/L (31.7 g/L SO_4) through crystallization of $Na_2SO_4 \cdot 10H_2O$; (ii) the solubility of Na_2SO_4 upon cooling is influences by the Cl^- concentration; (iii) the ROC process is most suitable for treatment of saline solutions rich in Na_2SO_4, as it can be precipitated through cooling as $Na_2SO_4 \cdot 10H_20$, followed by reverse osmosis to produce drinking water; (iv) The energy required to cool water, containing 100 g/L Na_2SO_4, from 25°C to 0°C, amounts to 10.66 kWh/t water. When 90% of the water is further cooled down to freeze 90% of the water, the energy consumption increased from 10.66 kWh/t to 37.74 kWh/t.

Acknowledgements

This work was made possible with the support of the following: The National Research Foundation, that have funded Tshwane University of Technology projects on effluent and solid waste treatment through their Technology and Human Resources for Industry Programme (THRIP); Rand Water for providing financial support for this research programme; and Prof. Fritz Carlsson is acknowledged for editing the manuscript.

Table 7
Effect of various parameters on the rate of ice crystallization and its purity

Exp no	Salt	Conc	Type	Bath temp	Strirring rate	Ice seed	Depth	Freezing time	Freezing Temp	Mass			Cl			Ca						Mg			Conuctivity			Ice rate	pH			Salt in ice
		~~m~~g/L		°C	rpm	g/L	cm	h	°C	g	g	g	ml/L	ml/L	ml/L	EDTA (ml)	EDTA (ml)	EDTA (ml)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mS/cm	mS/cm	mS/cm	g/(L.h)				%
										Feed	Brine	Ice	Feed	Brine	Ice	Feed	Brine	Ice	Feed	Brine	Ice	Feed	Brine	Ice	Feed	Brine	Ice		Feed	Brine	Ice	
	Time/Prog F C																															
1.1	MgSO4.7H2O	86.4	Prog F C	-10	270	0	5	**0.5**	-0.5	250	140	80										9 088	10 643	6 269	22.7	34.3	24.2	640				
1.2	MgSO4.7H2O	86.4	Prog F C	-10	270	0	5	**1**	-1	250	100	120										9 088	9 428	6 998	22.7	29.0	25.0	480				
1.3	MgSO4.7H2O	86.4	Prog F C	-10	270	0	5	**2**	-0.7	250	40	180										9 088	11 324	8 991	22.7	26.0	30.3	360				
	Time Susp F C																					0	0	0								
2.1	MgSO4.7H2O	86.4	Susp F C	-10	270	0	5	**0.5**	-0.5	250	80	180										9 817	10 449	8 019	27.8	32.6	28.2	1440				
2.2	MgSO4.7H2O	86.4	Susp F C	-10	270	0	5	**1**	-1	250	80	170										9 817	10 157	8 272	27.8	30.6	28.4	680				
2.3	MgSO4.7H2O	86.4	Susp F C	-10	270	0	5	**2**	-0.7	250	20	240										9 817	12 393	9 185	27.8	31.8	30.6	480				
	Rate of ice crystallization																					0	0	0								
3.1	MgSO4.7H2O	86.4	Susp F C	-10	250	10	5	1	-0.7	250	140	100										9 234	10 060	6 026	0.0	33.5	23.5	400				
3.2	MgSO4.7H2O	86.4	Susp F C	-10	250	10	2	1	-0.3	250	220	40										9 234	9 283	6 075	0.0	31.7	23.1	160				
	Ice seed crystal concentration																															
4.1	MgSO4.7H2O	86.4	Susp F C	-10	270	**0**	5	1	-1	250	224	32										7 290	7 047	10 352	26.5	28.0	26.0	128				
4.2	MgSO4.7H2O	86.4	Susp F C	-10	270	**10**	5	1	-1	250	167	114										7 290	12 344	7 630	26.5	34.0	21.2	456				
4.3	MgSO4.7H2O	86.4	Susp F C	-10	270	**30**	5	1	-1	250	168	104										7 290	12 296	7 290	26.5	31.7	18.7	416				
	Chemical																					0	0	0								%
5.1	**NaCl**	30	0	0	270	0	5	1	0	250	180	100	3 574	2 224	875										88.3	91.2	50.6		7.6	8.0	8.8	57
5.2	**CaCl2**	30	0	0	270	0	5	1	0	250	200	80	3 074	1 774	725	0.25	0.2	0.1	122	97	49				81.9	82.5	40.7		9.7	9.3	9.6	50
5.3	**MgSO4.7H2O**	30	0	0	270	0	5	1	0	250	140	100										5 783	6 318	2 867	22.0	22.1	11.8		7.3	7.7	7.7	54
5.4	**NaSO4**	30	0	0	270	0	5	1	0	250	160	120													65.2	41.6	49.6		8.0	8.3	8.1	76
5.5	**Al2(SO4)3**	30	0	0	270	0	5	1	0																9.0	9.0	7.1		3.4	3.4	3.4	79

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