Selectivity of ice crystallization and refrigeration waste heat integration in freeze desalination of brine – Application and Optimisation

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Abstract. Upon cooling, water reverts to its solid form – ice. Due to the small dimensions and lattice configuration of the ice crystal, inclusion of compounds in the crystal lattice is impossible. Mechanisms of contamination include; the interfacial tension between the small ice crystals and brine which causes the mother liquor to adhere to the crystal surface, interstitial entrapment of impurities between the ice crystals and pockets of impurities in the bulk crystal structure. The process of ice crystallisation is highly selective and therefore can be an important unit operation for the separation and purification of water. This unique property of ice is applicable to desalination of salt laden wastewaters (e.g. industrial brines) if the nucleation process is properly comprehended and controlled. Study on the bearing of various operating parameters on ice crystal purity was carried out, experimentally using synthetic (2-5% NaCl) and industrial brines, on a HybridICE™ pilot plant. Ice slurry was formed by circulating brine in a loop through cooled scraped surface heat exchangers. The ice in the slurry was then filtered off. Heat transfer, brine flow rate, ice scraping frequency and residence time in the filter, were the parameters used to counteract impurity entrapment mechanisms in ice during optimisation. Low value waste heat generated during the cooling process was used to evaporate the freeze concentrated brine under vacuum. Ice of 98% purity and distillate of 99.5% purity were obtained.

1. Introduction

Industrial brines have become one of the most problematic environmental pollutants in South Africa, with detrimental effects to both economic and social activities. The use of desalination technologies, like Reverse Osmosis (RO) and Electro-Dialysis (ED), which produce multi-component hypersaline brines, is acutely limited by inadequate waste brine disposal mechanisms such that the brine does not contaminate fresh water resources [1].

Currently, distillation and evaporation ponds are used as brine disposal methods. Distillation is energy intensive and evaporation ponds have a possibility of leaching soluble salts to the surrounding ground water. Freeze desalination has always been proven to be a viable technique to handle brines of elevated salinities [2]. The process is based on the principle that due to the small dimensions of the ice crystal lattice, inclusion of compounds in the crystal lattice is impossible except for flourhydric acid and ammonia [3]. The advantage of freeze desalination over distillation is that the latent heat of fusion of ice is 333 kJ/kg and that of evaporation of water is 2500 kJ/kg which implies significant energy savings [4].

Although the potential of freeze desalination processes is well documented and understood [5], there has not been any commercial breakthrough beyond pilot studies. The traditional barriers to the success of freeze desalination technologies include control and optimization of the crystallization process which is stochastic in nature [6] process complexity due to the need to grow the individual ice crystals [7], handling and transportation and of delicate ice slurries [8], separation of ice from mother liquor and ice washing in wash columns using a pressurized fresh water stream [9].

Ice crystal contamination is mainly due to interfacial tension and interstitial entrapment. Interfacial tension emanates from the high surface tension of water which results in adherence of brine to the ice crystal surface [10]. Interstitial entrapment on the other hand involves entrapment of impurities in spaces between individual or crystal clusters called interstices [11]. This form of impurity entrapment is mostly driven by the ice growth rate, freezing temperature and solute concentration in solution. High ice growth rates driven by high cooling rates favour the development of ice dendrites which trap dissolved solids as well as solids [12]. The irregular morphology of dendritic branched ice crystals result in the entrapment of pockets of highly concentrated brine within the ice matrix [13].

For freeze desalination technologies to break into the readily available market, novel and innovative designs are required to surmount these historical barriers. Mtombeni *et al.*, [14], achieved 98% ice purity using a newly developed freeze desalination process – the HybridICE – without washing the ice crystals. In this paper, a novel self-contained *Integrated* HybridICE™ process for zero liquid discharge is described. Factors affecting selectivity of the ice crystallization process, refrigeration waste heat recovery as well as optimization of operating parameters, are discussed.

2. HybridICE process description

The HybridICE process is a freeze desalination technology that utilizes the phase change of water (liquid to solid) to extract fresh water from salt laden waters by continuous crystallization on a cooled scraped surface. Brine is cooled indirectly in the scraped surface heat exchangers (SSHE) to a specific temperature and ice crystals form out of pure water molecules. A mixture of ice and brine (slurry) is formed and separated by an ice filter without the addition of fresh water to wash the ice crystals (Figure 1).

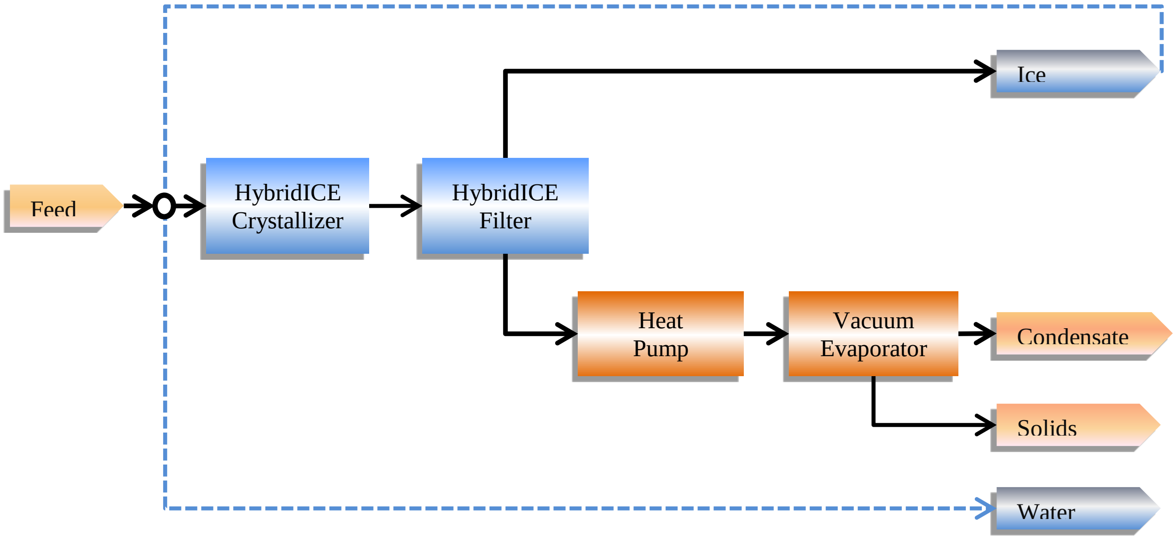

Figure 1: Integrated HybridICE process flow sheet

2.1. HybridICE process unit operations

The refrigeration unit (heat pump) extracts heat from and exhausts heat to the brine stream through evaporation or condensation of the refrigerant, respectively. The amount of ice formed is affected by the concentration of solute (freezing point depressant) in solution, the heat transfer coefficient and the differential temperature between the refrigerant and the brine as described by equation (1).

$$\dot{Q} = \dot{m}_b c_p dT + \dot{m}_i H_f \tag{1}$$

where $\dot{Q}$ is the cooling capacity of the refrigeration unit, $\dot{m}_b$ is mass flow rate of brine, $\dot{m}_i$ is the ice mass fraction in slurry, dT is change in brine temperature and H_f is the latent heat of fusion of ice (333 kJ/kg). In addition to effecting separation of ice crystals from brine concentrate, the HybridICE filter replaces the traditional ice growth tank. The ice crystals undergo recrystallization, Ostwald ripening and agglomeration to yield larger crystals which aid the removal of interstitial as well as interfacial brine. In the vacuum evaporator low value refrigeration waste heat is used to heat up the concentrate from the freeze crystallization stage. The heated concentrate is then evaporated under vacuum. A simple but versatile venture/educator pump is used to evacuate the evaporator. Steam condensate and salts are produced from the vacuum evaporator.

2.2. Heat pump principle

In Figure 2, the working fluid (refrigerant) evaporates at a lower absolute temperature T_e in the evaporator thereby extracting an amount of heat Q_e from the heat source. The gaseous refrigerant is then compressed and, as it condenses in the condenser, gives up an amount of latent heat Q_c at a higher absolute temperature T_c. From energy balance of the system;

$$Q_c = Q_e + W \tag{2}$$

where W is the input electrical energy needed to drive the compressor. The efficiency of a compressor driven heat pump is expressed as the coefficient of performance *(COP)*.

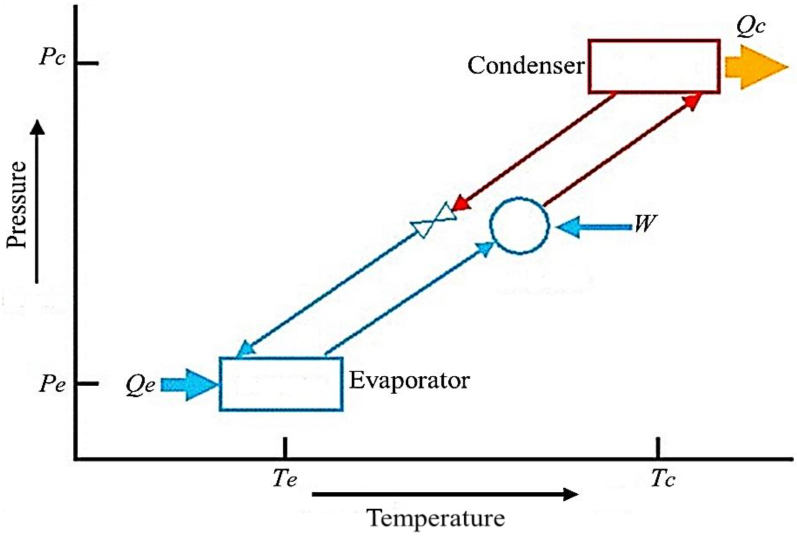

Figure 2: Temperature – pressure plot of a mechanical vapor compression heat pump

If both heating and cooling effects of the heat pump are employed, the thermal coupling yields:

$$COP_{Tot} = COP_H + COP_C \tag{3}$$

where COP_{Tot} is the total *COP* resulting from thermal coupling, COP_H is the heating *COP* and COP_C is the cooling *COP*. Therefore, from (2) and (3)

$$COP_{Tot} = \frac{Q_c + Q_e}{W} \tag{4}$$

From (2) it can be deduced that the heat delivered at the condenser Q_c is always greater than the heat removed from the evaporator Q_e. In conventional freeze desalination, refrigeration is applied to cool brine and drive ice nucleation only. Opportunities for using the waste heat (Q_c) should be interrogated since it is always greater than the cooling capacity (Q_e). The highest possible efficiency (COP) is achieved if both heat quantities are utilised simultaneously.

In a heat pump system, the temperature lift *(dT)* is the temperature differential between the condenser (heat sink) and the evaporator (heat source). This parameter determines the work input required to drive the process and can be deduced from Figure 2 as:

$$dT = T_c - T_e \tag{5}$$

Efficiency of a heat pump can also be theoretically calculated from the Carnot efficiency, COP_{TC} which is based on the temperature lift. COP_{TC} is the highest obtainable performance factor for any refrigeration system.

$$COP_{TC} = \frac{T_c}{T_c - T_e} \tag{6}$$

Combining (5) and (6) yields:

$$COP_{TC} = \frac{T_c}{dT} \tag{7}$$

This equation (7) demonstrates that the *COP* strongly depends on the temperature gradient *(dT)* between the heat source and the heat sink. High Total Dissolved Solids (TDS) brines have considerably low first-ice-points. This results in the compressor doing more work to move the heat.

3. Materials and methods

Batches of synthetic sodium chloride (2-5wt %) and industrial RO brines were treated using the HybridICE pilot plant. The impacts of scraper rotation speed, freeze temperature and feed flow-rate on energy consumption and ice purity were evaluated. Umetrics MODDE 9.1 package was used for optimisation of process parameters.

4. Results and discussion

The ice mass fraction in the slurry increases with increasing supercooling or as the freezing temperature decreases as shown in figure 3. This is attributable to the high freezing driving force at lower refrigerant temperatures as described by equation (1). High flow rates demand high cooling capacity to produce a given ice mass fraction. Ice fraction affects the ice residence time in the filter, hence overall process performance. The efficiency of the refrigeration system is affected by the temperature lift as shown in figure 4. More work is required to pump heat across large temperature gradients as shown by equation 9. High chloride removal was achieved using the HybridICE process during treatment of synthetic sodium chloride brines as shown in Figure 5. Low energy consumption shown in figure 6 is attributable to high freezing temperature of the brine which ranged from -1 to -3°C.

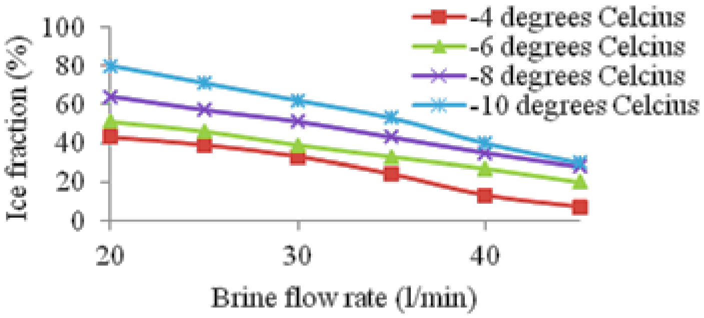

Figure 3: Effect of flow rate and freezing temperature on ice fraction (T_b = 20°C)

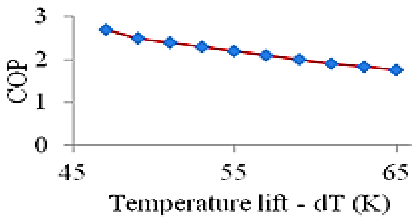

Figure 4: Effect of temperature lift on *COP*

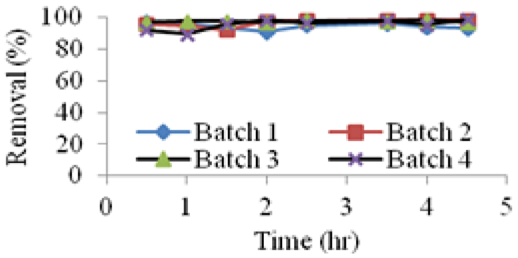

Figure 5: Chloride removal from sodium chloride based synthetic brine (2-5wt% NaCl)

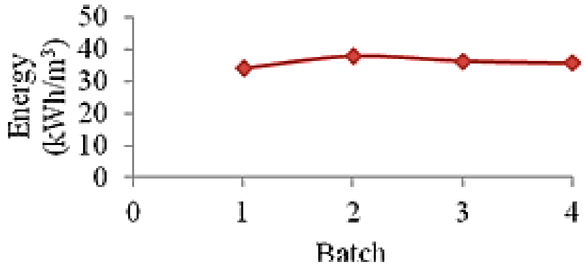

Figure 6: Energy consumption during treatment of sodium chloride synthetic brine (2-5wt% NaCl)

4.1. Optimisation (Umetrics MODDE 9.1)

The optimisation objective was to determine parameters that yield minimum energy consumption and maximum ice purity as shown in figures 7 and 8. Lower energy consumption was achieved at high freezing temperatures due to lower temperature lift (equation (9)). Ice purity is favoured by low ice fractions that are attainable at higher freezing temperatures and low flow rates.

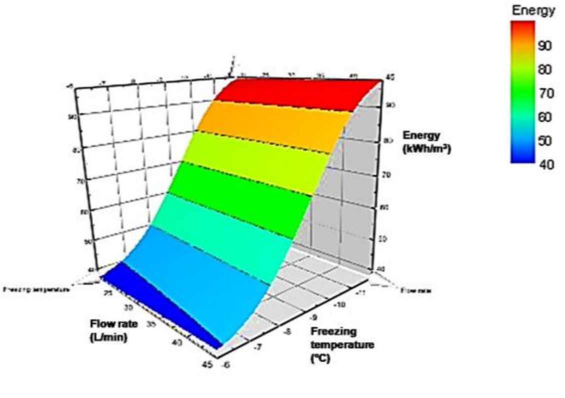

Figure 7: MODDE energy *minimization*

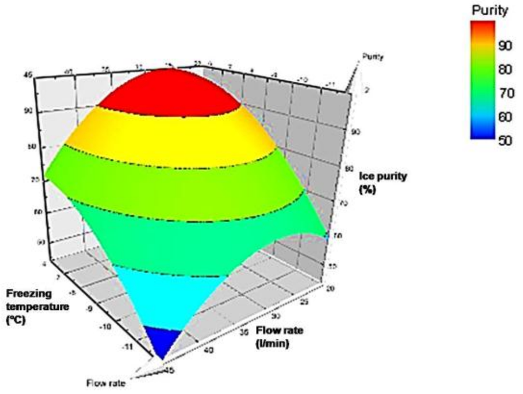

Figure 8: MODDE ice purity *maximization*

4.2. Industrial brine treatment

The parameters obtained during optimization were used in the treatment of an industrial brine stream. Impurity removal of 99% was achieved as shown in figure 9.

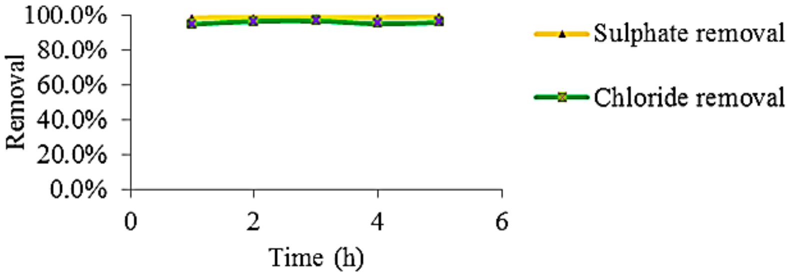

Figure 9: Impurity removal from industrial brine

5. Conclusion

The Integrated HybridICE freeze desalination process proved to be a novel technology capable of treating multi-component saline brines by employing the selectivity of ice crystallization.

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