

Moving towards a water-sustainable chemical industry: Novel water recovery processes

G. Kolliopoulos, E. Shum, J. Marial and V.G. Papangelakis*

Department of Chemical Engineering and Applied Chemistry, University of Toronto

* e-mail: vladimirospapangelakis@utoronto.ca

Abstract: A key factor to consider when thinking of a sustainable chemical industry that is using water in its operations (such as the metals and mining industry) is the energy footprint of the applied water recovery technologies. Forward Osmosis (FO) and Freeze Crystallization (FC) are two innovative processes promising to minimize fresh water intakes in the chemical industry at a significantly lower energy input compared to conventional processes, such as Reverse Osmosis (RO), evaporation, or crystallization. FO is a membrane process able to recover water from dilute feed solutions (i.e., industrial process water, high salinity streams), into a concentrated draw solution (CDS). The flow of water into the CDS occurs spontaneously, due to the osmotic pressure gradient generated between the two solutions, diluting the CDS. The draw solutes must then be separated from the resulting dilute draw solution (DDS) to regenerate and recycle the CDS in the process, leaving behind clean water. This step is the main source of energy consumption in the overall FO process, which only requires moderate heating. On the other hand, FC involves processes in which water is removed from an aqueous solution by freezing or freeze-thaw cycling, while the solutes remain in a concentrated aqueous phase from which they can be recovered or contained. The energy advantage is due to the fact that the latent heat of freezing is about 7 times lower than its evaporation analogue. Research advancements in the aforementioned processes are reported.

Key words: Water recovery, forward osmosis, natural freezing, freeze crystallization

1. INTRODUCTION

Currently in Ontario, Canada, around 2 million m³ of hazardous effluent streams are disposed off at an average cost of CAD\$ 115/m³. Recovering water from these streams by an energy efficient process presents several advantages: clean water production, which can be recycled in industrial operations, and reduced volumes of concentrated effluents that require disposal.

Desalination technologies such as membrane processes, (RO: Reverse Osmosis), and evaporative processes are energy intensive, and often limited to effluent streams with less than sea-like water concentration (Hancock, 2013). RO is more energy efficient at recovering water from low salinity streams, up to 35,000 ppm total dissolved solids (TDS). However, Forward Osmosis (FO) is more attractive compared to distillation or crystallization processes in recovering water from effluent streams of higher salinity, i.e., 60,000-240,000 ppm TDS, as the overall cost is significantly decreased (Kolliopoulos et al., 2016b). The FO process treatment window can be seen in Figure 1.

In FO, water molecules flow from a feed solution, i.e., an effluent stream, into an engineered concentrated draw solution (CDS) across the pores of a semi-permeable membrane that selectively allows this passage. This flow occurs spontaneously, due to the osmotic pressure gradient generated between the two solutions, and results in the recovery of water into the CDS. The latter gets diluted and must be treated to separate and recover the draw solutes from the product water. Energy requirements in FO arise from the separation and regeneration of the draw solution. Therefore, the draw solution selection impacts on the effectiveness of FO; an ideal draw solution must have high osmotic pressure and high volatility relative to water. Thermolytic salts present such properties and have been thoroughly studied as draw solutions in FO (Boo et al., 2015; Ge et al., 2013;

Kolliopoulos et al., 2015, 2016b, 2017; McCutcheon et al., 2005, 2006; McGinnis et al., 2007). Among these is aqueous carbonated trimethylamine (TMA), which was found to be superior in FO applications (Boo et al., 2015; Kolliopoulos et al., 2015, 2016a,b, 2017). The focus of this study is to determine the effectiveness and optimal operating conditions of the separation and regeneration of an aqueous carbonated TMA draw solution. The performance specifications selected for this study were: maximum of 200 ppm residual TMA in the recovered water, maximum energy consumption of 0.20 kWh per kg of H₂O produced, and 95% recovery of draw solutes.

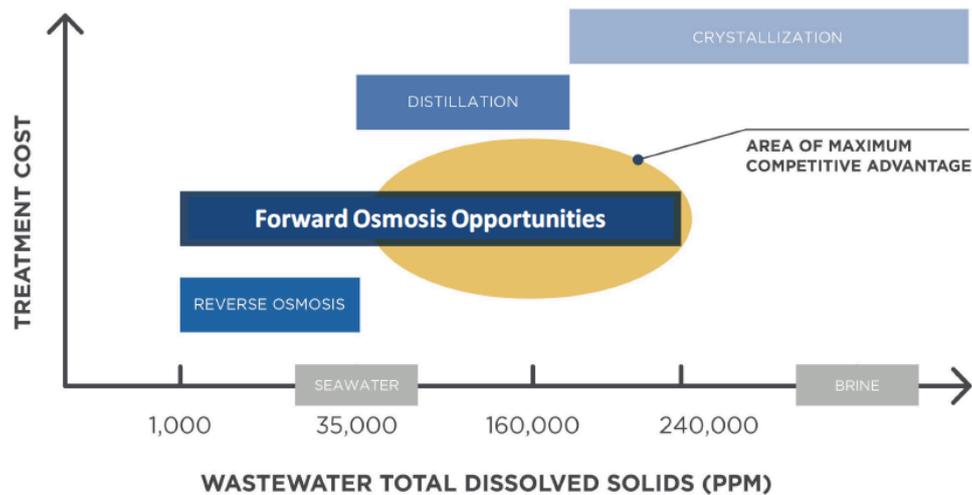


Figure 1. FO process treatment window (Kolliopoulos et al., 2016b)

Another promising technology to recover water from contaminated sources at a low energy footprint is “Freeze Crystallization” (FC). Advances in refrigeration technology have made low-temperature separation processes increasingly appealing to an energy-conscious society. The latent heat of water freezing is about seven times smaller than the latent heat of evaporation providing freezing with a strong thermodynamic advantage. The result is the development of a wide variety of processes called FC techniques, in which an aqueous solution is concentrated by the creation and subsequent removal of ice (Williams et al., 2015). FC processes exploit the freezing behaviour of aqueous solutions as dictated by the water-salt phase diagram. When, for example, a solution of magnesium sulfate is cooled to a temperature below its freezing point but above its eutectic temperature of $-4.1\text{ }^{\circ}\text{C}$ then, if the concentration of MgSO_4 is less than the eutectic concentration (about 1.7 molal), ice will form until the solution concentration reaches its equilibrium concentration at the given temperature on its phase diagram. If the concentration is greater than the eutectic concentration, MgSO_4 solid will precipitate until the concentration reaches equilibrium. Therefore, ice can be selectively produced in FC processes (Randall and Nathoo, 2015). Attempts to reduce energy requirements further resulted in the development of climate-induced techniques, i.e., “Natural Freezing”, to freeze and purify aqueous solutions. The principle is based on that of frozen lakes: a container filled with aqueous solution is left with its surface exposed to a sub-zero atmosphere. An ice layer forms on the surface, much like it would in nature, and grows in the direction of gravity (Hasan and Louhi-Kultanen, 2016). Although the objective of FC is to produce concentrated solution and pure ice, the presence of impurities trapped within the ice necessitates further processing to obtain pure water. It is believed that the thawing of ice crystals also releases solutes trapped between their grain boundaries (Mandri et al., 2011; Yee et al., 2004). Dendritic crystals beyond a given fineness -the result of high solute concentrations during ice growth requiring greater heat transfer- are too small to form channels, and instead melt away along with the trapped solution (Yee et al., 2003).

2. MATERIALS AND METHODS

2.1 Forward osmosis

The main source of energy consumption in the overall FO process arises from the separation and the regeneration of the draw solution. It has been shown that an FO process that uses stripping to separate the draw solution from the water recovered is the most economically efficient, with regards to the overall energy requirements of the process (Kolliopoulos et al., 2016a). Also, aqueous carbonated TMA has been identified as a very effective draw solution for both desalination and process water recovery via FO. Response Surface Methodology (RSM) was implemented as an optimization technique to identify the optimum operating conditions of the overall FO process; Aspen Plus (www.aspentech.com) and Minitab (www.minitab.com) were used in this computational study. There are two phases to the simulation work: the first one is the identification of the parameters that impact the stripping and regeneration steps, while the second involves the optimization of those parameters.

In the first phase, fractional factorial experiments were designed in Minitab. The experiments were then simulated in Aspen Plus using the model presented in Figure 2. An aqueous carbonated TMA draw solution is sent through an FO cell. The resulting dilute draw solution (DDS) is then sent to a stripping column, where TMA and CO₂ are stripped upon slight heating. Clean water is recovered and sent back into the process. The gaseous TMA and CO₂ go to an absorption column to regenerate the CDS.

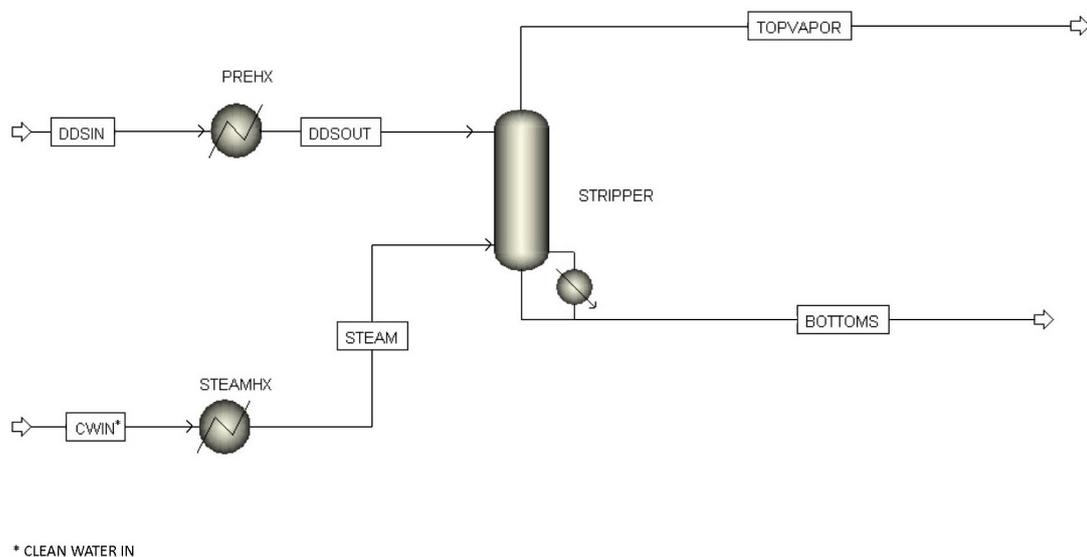


Figure 2. FO Process Aspen Model

The response data collected from Aspen was then imported into Minitab to identify the most important parameters at a confidence level of 95%. The parameters investigated include the number of stages (NS), feed to steam ratio (mass/mass) (FSR), column pressure (CP), feed temperature (FT), feed dilution factor (FDF) and steam temperature (ST).

In the second phase, the optimization experiments were designed in Minitab using the RSM package; Central Composite Design (CCD) was used. The experimental design from Minitab was used to obtain the response data in Aspen Plus. The latter was then imported back into Minitab for the regression analysis, which was completed by considering each adjustable variable at time. The optimization goals were entered into Minitab, to locate the best setting of the important parameters. Finally, a simulation at the optimal conditions was carried out in Aspen Plus to obtain the results when operating at the optimum set of conditions.

2.2 Natural freezing

Natural freezing was simulated by placing heat exchangers and a fan in a Styrofoam box. Coolant from a refrigerating circulator passed through the heat exchangers, and the temperature in the box was regulated by means of a Pt100 temperature probe connected to the refrigerating circulator. A 500 mL of 0.5 molal MgSO_4 solution was placed in a silicone container insulated on the sides and bottom with Styrofoam to present only the surface of the solution to the cold air. The temperatures tested ranged from $-1\text{ }^\circ\text{C}$ to $-6\text{ }^\circ\text{C}$, and the solution was frozen for four days. After freezing, the ice was removed and washed with 100 mL of chilled deionised water (Hasan and Louhi-Kultanen, 2016). The ice was then either left to melt at room temperature or placed right-side-up on a metal plate heated to $50\text{ }^\circ\text{C}$, which caused the solid that grew last to melt first. The run-off from melting was periodically collected. All liquid collected was then diluted to fixed volumes. Analysis was performed via ICP-OES on the molten ice, the concentrated solution left behind in the container, and the rinse water in order to measure the magnesium content.

3. RESULTS AND DISCUSSION

3.1 Forward osmosis

The main optimization objectives were: maximum of 200 ppm of TMA in the recovered water, at most 0.20 kWh/kg of H_2O produced, and 95% recovery of draw solutes. Important Parameters that impact the effectiveness of the stripping step were identified: FSR, FT, ST, and FDF. It was found that the number of stages and column pressure did not have a significant impact on the separation of TMA and CO_2 . The latter can be explained by the big difference between the boiling points of TMA and CO_2 . Therefore, $\text{NS}=2$, and $\text{CP}=1\text{ atm}$, since this is the minimum value requirement by a Radfrac Model in Aspen Plus, and the most economical operation setting for a column, respectively. The Radfrac model is the main separation block in Aspen Plus, used to simulate column separation. The important parameters were then optimized with respect to the recovery of draw solutes and the total process energy consumption; their optimal settings and the corresponding values for the response parameters are summarized in Table 1a-b.

Table 1. Optimization results

a. Optimal settings for the most important parameters			
Parameter	Value		
FSR (g/g)	4.13		
FT ($^\circ\text{C}$)	20		
ST ($^\circ\text{C}$)	110		
FDF	2.75 (13.8 wt.% TMA, 9.2 wt.% CO_2 , balance: H_2O)		
b. Comparison of Aspen Plus and Minitab models for the response variables at the optimal conditions			
Variable	Aspen Values	Minitab Values	Target Values
TMA Concentration in Recovered Water (wt.%)	0.77	0.047	0.07
TMA Concentration in Top Vapor Stream (wt.%)	49.54	42.99	35
CO_2 Concentration in Top Vapor stream (wt.%)	33.28	26.44	23
% Recovery of TMA	93.93	99.36	100
Energy Consumption (kWh/kg)	0.29	0.24	0.20

Generally, there is good agreement between the data obtained from Aspen Plus and Minitab. The only major discrepancy is observed in the TMA level in the bottoms stream of the stripping column, where the values obtained differ by one order of magnitude. This discrepancy was attributed to the optimization process being done in Minitab, and not directly in Aspen Plus, which has thermochemical property models and is able to calculate mass balances with a considerable degree of accuracy.

3.2 Natural freezing

From the raw data collected, the amount of water frozen and magnesium sulfate solution entrapped in the ice were measured. Furthermore, the cumulative effect of freezing was calculated by measuring discrete volumes of solid melt. From this data the cumulative molality of the remaining un-melted ice was plotted against the percentage of the initial water remaining in the ice.

From an initial concentration of ~ 0.5 molal MgSO_4 it was possible to produce ice nearly fifteen times purer (from 0.5 molal to virtually no magnesium sulfate). It was found that experiments where the ice was melted by means of a heated plate resulted in increased magnesium concentration vs. water recovery, while experiments where the ice was allowed to melt at room temperature (labelled SM on Figure 3) had significantly lower magnesium concentrations. The trade-off was that while it took roughly 1 h to melt the ice produced using a heated place, it took roughly 3 h to melt a similar mass of ice at room temperature. Furthermore, high rates of water recovery inevitably resulted in increasingly impure ice. The water recovery percentage for the -1°C heated plate experiment ends at $\sim 30\%$ because a much lower amount of solution was frozen after four days compared to the other experimental runs.

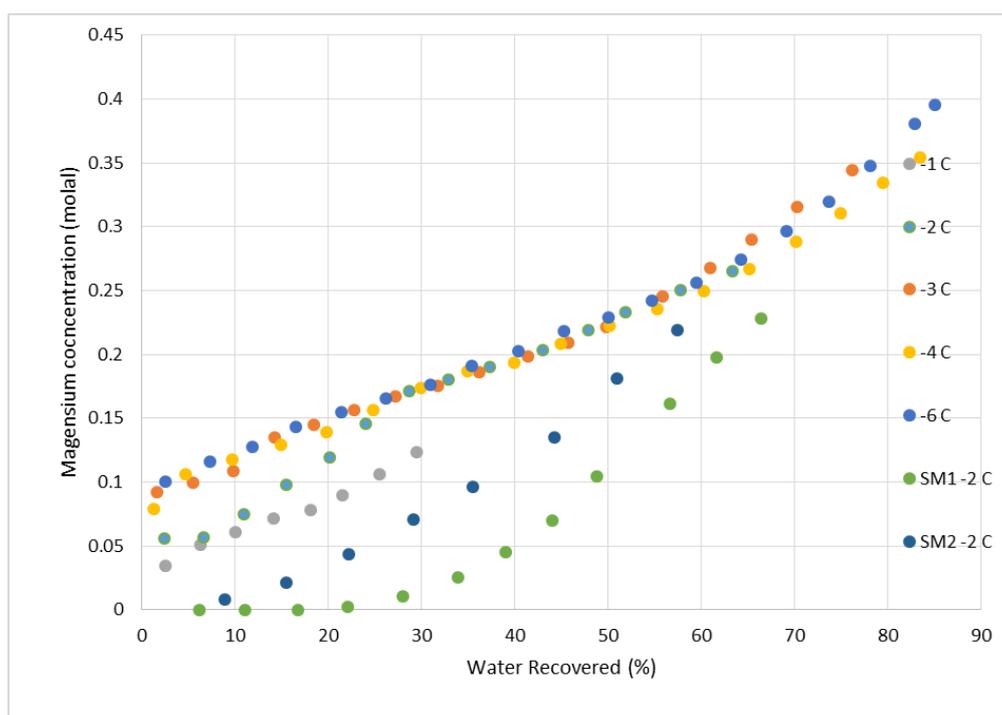


Figure 3. Magnesium concentration of solid plotted against water recovered as ice

Although it was expected that lower temperatures would result in the production of ice with more impurities as increased speed of ice growth would result in greater entrapment of magnesium sulfate solution, it was found that an air temperature of -3 , -4 , and -6°C resulted in concentration/ice production profiles that were virtually identical in appearance (Figure 3). However, for air temperatures of -1 and -2°C it was found that warmer temperatures (close to the solution liquidus temperature of $\sim -0.8^\circ\text{C}$) resulted in lower concentrations of solid.

The slow melting of ice at room temperature dramatically decreased the magnesium concentration at higher water recovery rates, with $\sim 25\%$ water recovery at a magnesium concentration of nearly zero molal in one experimental run. It is believed that this is due to the fact that slower melting allows for the entrapped solute to drain from between the grain boundaries of ice crystals, leaving behind purer ice. This effect is lost at higher temperatures when the ice crystals melt at rates similar to the draining of entrapped solute.

4. CONCLUSIONS

The most important parameters were identified to be FSR, FT, ST, and FDF; NS and CP were identified to have insignificant impact on the degree of separation. The optimal conditions were identified as a FSF=4.13, FT=20 °C, ST=110 °C, and FDF=2.75. The current set up in Aspen Plus makes a strong case for low capital cost, due to the low number of required stages and the near ambient operating pressure. It is apparent that the required energy input is somewhat higher (0.29 kWh/kg) than the targeted one (0.20 kWh/kg). However, in this setup no waste heat integration was considered; in another setup that would incorporate waste heat integration, the energy requirements of the FO process are expected to decrease significantly.

The application of freezing technology towards the recovery of water is still in its relative infancy. However, it is evident that the process of applying natural freezing towards the recovery of water by freeze concentration does result in the production of ice that is purer than the original solution. This effect is further enhanced by the thawing at room temperature of the ice produced by natural freezing, which allows entrapped solute to drain away. Current experiments can recover nearly 25% of the original water at very low magnesium sulfate concentrations, leaving behind a more concentrated solution. As the extent of pure water recovery appears to be linked to the thawing temperature, further experiments are to be conducted to increase water recovery, thereby increasing the concentration of the remaining solution to the point where it can be treated using conventional processes.

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REFERENCES

- Boo, C., Khalil, Y.F. and Elimelech, M., 2015. Performance evaluation of trimethylamine-carbon dioxide thermolytic draw solution for engineered osmosis. *Journal of Membrane Science*, 473(0): 302-309.
- Ge, Q., Ling, M. and Chung, T.-S., 2013. Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future. *Journal of Membrane Science*, 442(0): 225-237.
- Hancock, N., 2013. Engineered Osmosis for Energy Efficient Separations: Optimizing Waste Heat Utilization Final Scientific Report DOE F 241.3. DOE/EE003467-1 United States 10.2172/1067379 GFO English; Oasys Water Inc, Boston, MA.
- Hasan, M. and Louhi-Kultanen, M., 2016. Water purification of aqueous nickel sulfate solutions by air cooled natural freezing. *Chemical Engineering Journal*, 294: 176-184.
- Kolliopoulos, G., Carlos, M., Clark, T.J., Holland, A.M., Peng, D.-Y., Papangelakis, V.G., 2017. Chemical Modeling of the TMA-CO₂-H₂O System: A Draw Solution in Forward Osmosis for Process Water Recovery. *Journal of Chemical & Engineering Data*, 62(4), 1214-1222
- Kolliopoulos, G., Carlos, M., Holland, A.M., Clark, T.J. and Papangelakis, V.G., 2016a. Forward Osmosis for Process Water Purification Using Carbonated Trimethylamine as the Draw Solution, *Water in Mining 2016*, Proceedings of the 5th International Congress on Water Management in Mining, J. Wiertz, N. McIntyre (eds.) May 18-20, 2016, Paper No. 71. Santiago, Chile.
- Kolliopoulos, G., Clark, T. and Papangelakis, V.G., 2015. Forward Osmosis for Industrial Process Water Recovery: The Case of TMA-CO₂-H₂O as Draw Solution, COM 2015 | The Conference of Metallurgists hosting AMCAA | America's Conference on Aluminum Alloys, August 23-26, 2015, Canadian Institute of Mining, Metallurgy and Petroleum (CIM), Paper No. 8991, Toronto, ON, Canada.
- Kolliopoulos, G., Karlov, A., Holland, A.M., Clark, T.J. and Papangelakis, V.G., 2016b. Forward Osmosis: A Promising Process for Industrial Process Water Recovery, 77th Annual International Water Conference (IWC), November 6-10, 2016, Engineers' Society of Western Pennsylvania (ESWP). Paper No. IWC 16-29. San Antonio, Texas, USA.
- Mandri, Y. et al., 2011. Parametric study of the sweating step in the seawater desalination process by indirect freezing. *Desalination*, 269(1-3): 142-147.
- McCutcheon, J.R., McGinnis, R.L. and Elimelech, M., 2005. A novel ammonia-carbon dioxide forward (direct) osmosis desalination process. *Desalination*, 174(1): 1-11.
- McCutcheon, J.R., McGinnis, R.L. and Elimelech, M., 2006. Desalination by ammonia-carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. *Journal of Membrane Science*, 278(1-2): 114-123.

- McGinnis, R.L., McCutcheon, J.R. and Elimelech, M., 2007. A novel ammonia–carbon dioxide osmotic heat engine for power generation. *Journal of Membrane Science*, 305(1–2): 13-19.
- Randall, D.G. and Nathoo, J., 2015. A succinct review of the treatment of Reverse Osmosis brines using Freeze Crystallization. *Journal of Water Process Engineering*, 8: 186-194.
- Williams, P.M., Ahmad, M., Connolly, B.S. and Oatley-Radcliffe, D.L., 2015. Technology for freeze concentration in the desalination industry. *Desalination*, 356: 314-327.
- Yee, P.L., Wakisaka, M., Shirai, Y. and Hassan, M.A., 2003. Effects of Single Food Components on Freeze Concentration by Freezing and Thawing Technique. *Nihon Shokuhin Kougakukaishi (Japan Journal of Food Engineering)*, 4(3): 77-83.
- Yee, P.L., Wakisaka, M., Shirai, Y. and Hassan, M.A., 2004. Effect of Sodium Chloride on Freeze Concentration of Food Components by Freezing and Thawing Technique. *Nihon Shokuhin Kougakukaishi (Japan Journal of Food Engineering)*, 5(2): 97-103.