FREEZING YOUR BRINES OFF: EUTECTIC FREEZE CRYSTALLIZATION FOR BRINE TREATMENT

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ABSTRACT

Eutectic Freeze Crystallization (EFC) offers a novel method of treating brines and concentrates in order to recover pure water and salt. Because the heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol), the energy required to separate the water as ice is significantly less than that required to separate it by evaporation. However, the energy costs for freezing will be dominated by the cost of electricity to the compressor as opposed to heating costs for Evaporative Crystallization which depend primarily on the steam requirement.

This paper presents an EFC brine treatment protocol developed by the Crystallization and Precipitation Unit at the University of Cape Town for the treatment of multi-component, hypersaline brines. The protocol incorporates brine analysis, thermodynamic modelling to establish which salts will freeze out and at which temperatures and experimental studies to determine the kinetic parameters such as nucleation temperatures, salt yields and crystal purity. A preliminary economic evaluation based on two typical mine water brines containing high levels of sodium, sulphate and chloride was carried out to provide an approximation of the expected operating and capital costs associated with using EFC and these were compared to triple-effect evaporative crystallization (EC).

The operating cost savings of using EFC over EC were 80% and 85% for Brine 1 and Brine 2 respectively. The cost savings of using EFC could potentially be further enhanced by incorporating the income generated from the sale of the pure salts produced by the EFC process, as well as accounting for the additional mixed salt disposal costs for EC. The capital equipment costs for treating 100m^3/day of brine using EFC was R7.9 million and R12.1 million for Brine 1 and 2 respectively. In comparison, the capital costs for treating the same volume of brine using EC was R4.4 million and R5.8 million for Brines 1 and 2. Although the Eutectic Freeze Crystallization capital costs are significantly higher than those for Evaporative Crystallization, EFC is a new process with significant room for technology improvements and thus capital cost reductions. Conversely, EC is well established, with only incremental future equipment cost savings expected as a result of any further improvements in the existing technology.

1. INTRODUCTION

The two major problems currently facing South African water users are the declining availability of sufficient quantities of water and the deterioration of the quality of the available water (Buckley, 2005). Current water treatment processes including water recovery though desalination, ion exchange regeneration and membrane treatments all generate saline effluents that require additional handling and disposal. Handling of these hypersaline brines for additional water recovery and further reduction of the waste streams via a concentration process such as Evaporative Crystallization is energy intensive and thus costly.

Eutectic freeze crystallisation (EFC) is an alternative technology for the separation of highly concentrated aqueous streams. EFC is a technique that is capable of separating aqueous solutions into pure water and pure, solidified solutes (van der Ham, 2002). Because the heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol), the energy required to separate the water as ice is significantly less than that required to separate it by evaporation making EFC highly energy efficient. In addition, the simultaneous production of pure ice and pure salt(s) is a major advantage.

Although EFC has been shown to be effective in separating a single salt and water, its technical and economic feasibility has yet to be ascertained for complex hypersaline brines that are typical of reverse osmosis retentates in South Africa. This paper introduces the EFC brine treatment protocol developed by the Crystallization and Precipitation Unit at the University of Cape Town for the treatment of multi-component, hypersaline brines and subsequently presents a preliminary operating and capital cost based economic evaluation of this novel technology for the treatment of two sample brines that are broadly representative of South African industrial brines. A comparison of the preliminary operating and capital costs associated with treating the two sample brines using EFC with those for treating the brines with triple-effect evaporation (EC) is also presented.

2. BACKGROUND

Principle of Eutectic Freeze Crystallization

The principle of the process is as follows: when a solution containing dissolved contaminants is slowly frozen, water ice crystals form on the surface, and the contaminants are concentrated in the remaining solution (the mother liquor) (Gartner et al, 2005). The ice crystals can be separated from the mother liquor, washed and melted to yield a nearly pure water stream. The mother liquor will contain a pure salt, which crystallizes at the eutectic temperature. Theoretically, a 100% yield can be obtained in a binary system, which is one of the advantages of EFC technology. The level of accumulation of impurities can be controlled by means of purge streams (Vaessen, 2003).

3. BRINE TREATMENT PROTOCOL

The primary function of the brine treatment protocol developed by the Crystallization and Precipitation Unit at the University of Cape Town is to establish the technical feasibility and the key EFC operating parameters for a brine based on its chemical composition. This information can then be used to develop a process flow sheet and to calculate the operating and capital costs in order to evaluate the economic feasibility of applying EFC.

The protocol incorporates a comprehensive brine analysis, thermodynamic modelling, and experimental studies to determine kinetic parameters. Each of these individual steps is described in further detail below:

Brine analysis

A comprehensive and accurate chemical analysis of the multi-component brine is an essential pre-requisite for accurately simulating and optimising an EFC process based on thermodynamics. The thermodynamic calculations require the stream to be charge-neutral. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and/or Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Ion Chromatography (IC) are typically used to measure the cations and the anions respectively. In addition to this, the total alkalinity is determined using the extended Gran Theory method (Loewenthal et al., 1989) and the total organic and the inorganic nitrogen determined by the Total Kjeldahl Nitrogen (TKN) method of analysis.

Thermodynamic modelling

Due to the limited availability of solubility data especially for complex, multi-component brines, a thermodynamic modelling tool such as OLI Stream Analyser, developed by OLI Systems Inc (2008) is used investigate the phase equilibria associated with the EFC process. In particular, the temperatures at which the individual salts crystallize out and the predicted recoveries can be determined. The OLI software uses the Helgeson-Kirkham-Flowers (HKF) model for the calculation of the standard properties of the aqueous species. The excess terms are calculated based on the frameworks of Bromley, Zemaitis, Pitzer, Debye-Huckel and others.

Experimental validation

Whilst the thermodynamic modelling provides information on the thermodynamic feasibility of using EFC to treat a specific brine together with the predicted crystallization temperatures and salt recoveries, an experimental validation of these parameters needs be carried out in order to account for kinetic considerations such as the metastable zone width for the EFC process. The experimental validation to establish the individual crystallization temperatures for the individual salts, the eutectic temperatures, the various salt yields and recoveries and metastable zone widths are carried out batch wise in a 2.5L scraped, cooled wall crystallizer with inline measurements and data logging of the temperature and the conductivity profiles within the crystallizer. The experimental validation process also includes establishing the purity of the ice and salts produced.

4. DEVELOPMENT OF AN EFC PROCESS FLOWSHEET BASED ON THERMODYNAMIC MODELLING

The development of an EFC process flow sheet is illustrated by means of two case studies which are based on reverse osmosis retentates from typical mine water brines containing high levels of sodium, sulphate and chlorine. The chemical composition of the Brine 1 and Brine 2 that were used in case study 1 and 2 respectively are given in Table 1.

Table 1**.** Composition of Brine 1 and Brine 2

Brine 1		**Brine 2**	
Ions	Concentration [mg/L]	Ions	Concentration [mg/L]
Cl^-	2260	Cl^-	80800
SO_4^{2-}	7440	SO_4^{2-}	37400
Na^+	5027	Na^+	70300

Thermodynamic Predictions of Salt and Ice Crystallization Temperatures

The prediction of salt and ice crystallization was carried out using OLI Stream Analyser due to its ability to accurately simulate aqueous chemistry at high ionic strengths.

Figure 1 below shows the prediction of the successive crystallization of the various salts for 1 litre of Brine 1 with a reduction in the solution temperature from right to left on the x-axis. The results show that once the temperature reaches 0˚C ice crystallizes out, followed by $Na_2SO_4.10H_2O$ at -1˚C and $NaCl.2H_2O$ at -23˚C.

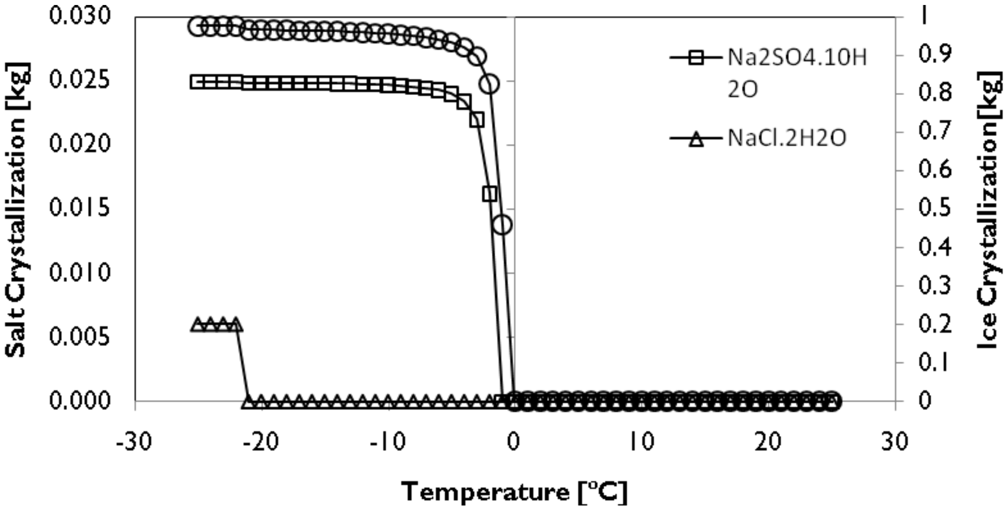

Figure 1. Thermodynamically predicted salt and ice crystallization temperatures for Brine 1 (Basis = 1 litre of brine)

Figure 2 shows the prediction of the successive crystallization of the various salts for Brine 2 with a reduction in the solution temperature from right to left on the x-axis. The results show that once the temperature reaches 14˚C $Na_2SO_4.10H_2O$ crystallizes out, followed by ice at -9˚C and $NaCl.2H_2O$ at -21˚C.

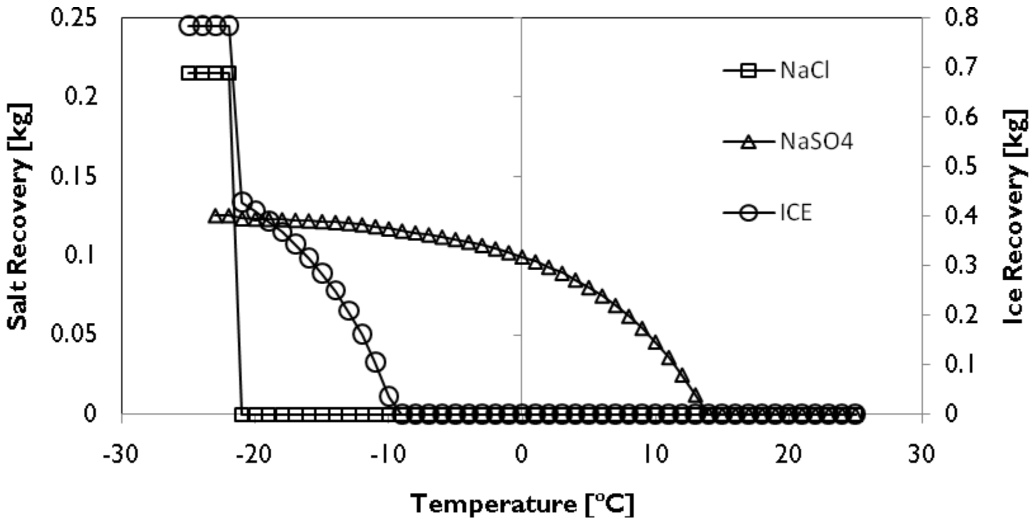

Figure 2. Thermodynamically predicted salt and ice crystallization temperatures for Brine 2 (Basis = 1 litre of brine)

Selecting the Operating Temperatures for the EFC Process

Based on the thermodynamic modelling results shown in Figure 1 and Figure 2 there are two distinct operating regimes for both brines where, sequentially, the ice and $Na_2SO_4.10H_2O$ can be crystallized out in the first crystallizer operating at a higher temperature followed by ice and $NaCl.2H_2O$ in the second crystallizer operating at a lower temperature.

For Brine 1 the operating temperature for the first freeze crystallizer was selected to be -5˚C in order to maximise the $Na_2SO_4.10H_2O$ recovery and to ensure sufficient under-cooling for kinetic reasons. The operating temperature for the second, lower temperature crystallizer was set at -23˚C.

For Brine 2 the operating temperature for the first freeze crystallizer was selected to be -15˚C in order to maximise the $Na_2SO_4.10H_2O$ recovery and to ensure sufficient under cooling for kinetic reasons. The operating temperature for the second, lower temperature crystallizer was set at -23˚C.

EFC Process Flow Sheet

Based on the selected operating temperatures for the EFC process, the following basic sequential EFC process flow sheet was developed:

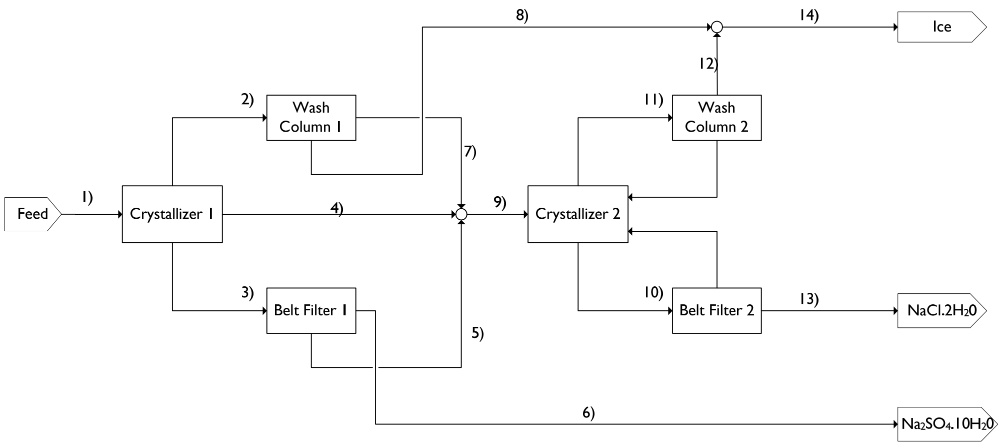

Figure 3. Basic sequential EFC process flow sheet for Brines 1 and 2

Three steams leave the first crystallizer. Of the three, the ice stream is sent to a wash column to wash off any brine that is entrained within the ice crystals, the salt stream that is sent to a belt filter to dewater the salt and third stream consisting of the remaining brine fed to the second crystallizer. Similarly, the ice and salt produced in the second crystallizer are sent to a wash column and belt filter.

5. PRELIMINARY COSTS AND BENEFITS OF APPLYING EFC

A preliminary economic evaluation was carried out to provide and approximation of the expected operating and capital expenditure costs associated with using EFC to treat Brine 1 and Brine 2. Owing to the fact that, by and large, the largest operating cost for an EFC process is the electricity requirement for the compressor in the refrigeration unit that is used to cool down the brine stream, this was used as the principal basis for evaluating the operating cost for EFC.

An economic evaluation using evaporative crystallization as an alternative treatment method to EFC is presented for comparison purposes. Whilst both EFC and evaporative crystallization significantly reduce the volume of the brines that would otherwise need to be stored in evaporation ponds, it is important to note that for a mixture of salts, EFC has the potential to separate the salts into pure products that can be sold and the income generated from the sale of these salts used to offset the operating costs. In contrast, evaporative crystallization typically produces a mixed salt, which subsequently needs to be disposed of - further adding to the operating cost. Furthermore, the revenue obtained by the sale of the pure salts produced by EFC is not included in this study.

EFC Operating Cost Approximation

The EFC operating cost was based on the refrigeration system compressor duty for a single-stage refrigeration system. For both brines, ammonia was used as the refrigerant and an isentropic efficiency of 75% was used for the compressor based on state of compressor technology currently.

For a $100m^3$/day Brine 1 stream, with the first and second freeze crystallizers operating at -5˚C and -23˚C respectively, a summary of the rate of production of ice and salts, the respective cooling duties and the associated costs based on an electricity cost of R0.39/kWh are shown in Table 2:

Table 2**.** Summary of the respective cooling duties and the rate of production of ice and salts for $100m^3$/day of Brine 1

	Crystallizer 1 (-5˚C)	**Crystallizer 2 (-23˚C)**
$Na_2SO_4.10H_2O$ produced [kg/hr]	104	-
$NaCl.2H_2O$	-	25
Ice produced [kg/hr]	3912	178
Cooling Duty [kW]	504	19
Compressor Duty [kW]	239	9
Cost/day [R/day]	R 2236	R 86

Cost/m^3 of brine[R/m^3]	R 22	R 0.9
Total operating cost for 100m^3/day: R 2322/day or R 23/m^3		

For a 100m^3/day Brine 2 stream, with the first and second freeze crystallizers operating at -15˚C and -23˚C respectively, a summary of the rate of production of ice and salts, the respective cooling duties and the associated costs based on an electricity cost of R0.39/kWh are shown in Table 3:

Table 3**.** Summary of the respective cooling duties and the rate of production of ice and salts for 100m^3/day of Brine 2

	Crystallizer 1 (-5˚C)	**Crystallizer 2 (-23˚C)**
$Na_2SO_4.10H_2O$ produced [kg/hr]	554	-
$NaCl.2H_2O$	-	952
Ice produced [kg/hr]	1219	2266
Cooling Duty [kW]	345	245
Compressor Duty [kW]	164	116
Cost/day [R/day]	R 1531	R 1087
Cost/m^3 of brine[R/m^3]	R 15	R 11
Total operating cost for 100m^3/day: R 2618/day or R 26/m^3		

Operating Cost for Triple-Effect Evaporative Crystallization

The operating costs for treating 100m^3/day of Brine 1 and 2 using a triple-effect evaporative crystalliser operating at 111˚C based on a cost of the steam of R0.27/kg (350kPa) are shown in Table 4:

Table 4. Summary of the heating duties and associated costs for EC

	Brine 1	**Brine 2**
Steam (water) production rate [kg/hr]	4170	4190
Heating duty [kW]	3140	4840
Cost/day [R/day]	R 11400	R 17500
Cost/m^3 of brine[R/m^3]	R 114	R 175

Comparing the Estimated Operating Costs for EFC with Triple-Effect Evaporative Crystallization

Figure 4 below shows the daily operating cost comparison between the EFC and triple-effect evaporative crystallization (EC) for Brines 1 and 2 based on the electricity cost for the compressor in the refrigeration unit for EFC and the cost of steam for evaporative crystallization.

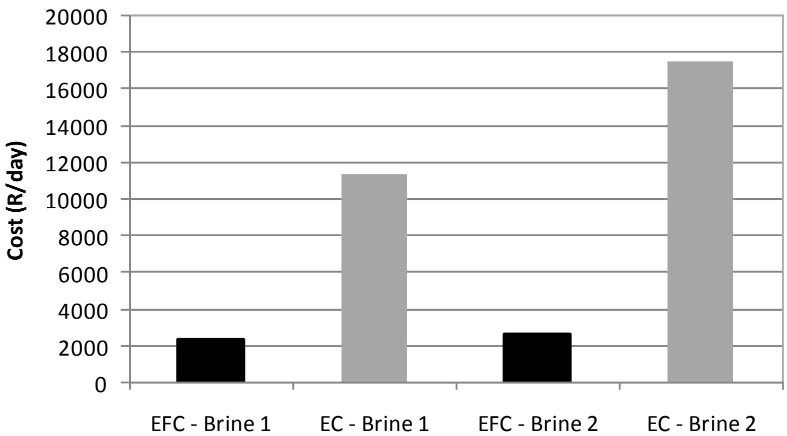

Figure 4**.** Comparison of daily operating costs for treating Brines 1 and 2 with EFC and multi-stage evaporation (Basis = 100m^3/day of brine)

When comparing the approximated operating cost of EFC with EC it is evident that EFC is significantly more cost effective than EC. The cost saving of using EFC over EC is of 80% and 85% for Brine 1 and Brine 2 respectively. Moreover, this preliminary operating cost evaluation does not incorporate possible heat integration between the ice produced and the feed to the EFC crystallizer or to cool the condenser in a 2-stage refrigeration system. In addition, the revenue generated by the sale of the pure salts produced by EFC and the cost of disposal of the mixed salt produced by EC are not included in this study.

Estimated Capital Costs for EFC and EC

The investment costs for treating Brine 1 and Brine 2 using EFC were calculated in accordance with the semi-empirical method described by Vaessen (2003). The EFC investment costs for treating these brines were then compared to evaporative crystallization (EC). There are limitations to the level of accuracy with which the investment costs for a full scale plant based on a relatively new technology such as EFC can be determined. Nonetheless, the scope of this study was to generate an order of magnitude estimate that can be used to compare the costs of implementing EFC versus those for EC.

Figure 5 below shows a comparison of the capital equipment costs for EFC and EC.

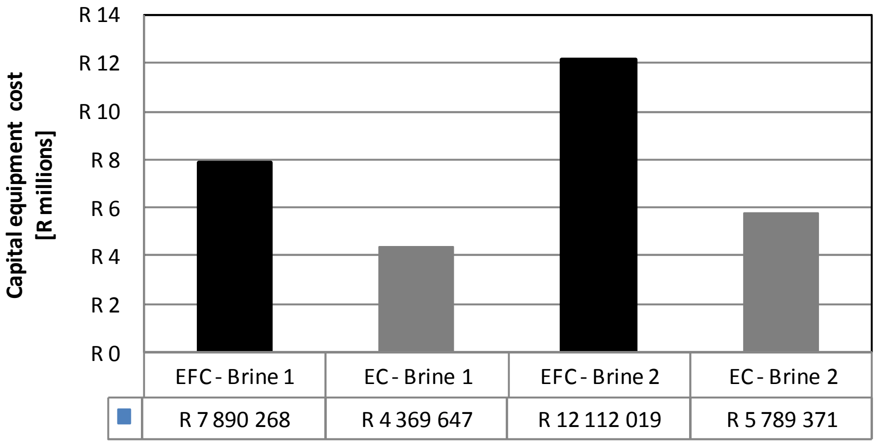

Figure 5. Comparison of the capital cost of equipment for Brines 1 and 2 for EFC and EC (Basis = $100m^3$/day of brine)

As expected the capital costs for EFC, which is a relatively new technology, are 88% and 91% more than that for a triple effect EC process for Brines 1 and 2 respectively. However, it is important to note that the capital cost calculations for EC are based on a technology that is already well established, with only relatively marginal future equipment cost savings expected as a result of improvements in the existing technology. In contrast, EFC is a new technology with future improvements expected in the technology resulting in capital cost reductions in particular with regards to the EFC reactor.

6. CONCLUSIONS

- Two brines broadly representative of typical South African mine water and industrial brines i.e. consisting of Na_2SO_4 and NaCl were investigated. The concentration factor difference between the two brines was approximately 10 with Brine 2 being more concentrated than Brine 1. A basis of $100m^3$/day of brine was used.
- For Brine 1 the thermodynamic modelling predicted that ice crystallizes out at 0˚C, followed by $Na_2SO_4.10H_2O$ at -1˚C and $NaCl.2H_2O$ at -23˚C. For Brine 2 $Na_2SO_4.10H_2O$ crystallizes out at 14˚C, followed by ice at -9˚C and $NaCl.2H_2O$ at -21˚C. Based on these temperatures the first and second crystallizers were respectively operated at -5˚C and -23˚C for Brine 1 and -15˚C and -23˚C for Brine 2 .
- The operating cost calculated for using EFC to treat Brine 1 with a cooling requirement of 523kW was $R23/m^3$. In contrast, the operating cost for a triple-effect EC process to treat Brine 1 with a heating duty requirement of 3140kW was $R114/m^3$.
- The operating cost calculated for using EFC to treat Brine 2 with a cooling requirement of 590kW was $R26/m^3$. In contrast, the operating cost for a triple-effect EC process to treat Brine 2 with a heating duty requirement of 4840kW was $R175/m^3$.
- Hence, the operating cost savings of using EFC over EC are 80% and 85% for Brine 1 and Brine 2 respectively. The cost savings of using EFC could potentially be further enhanced by incorporating the revenue generated from the sale of the pure salts produced by the EFC process, as well as taking into consideration the additional mixed salt disposal costs for EC.
- The capital equipment cost for EFC for treating $100m^3$/day of Brine 1 and Brine 2 was R7.9 million and R12.1 million respectively. In comparison, the capital costs for treating the same volume of brine using EC was R4.4 million and R5.8 million for Brine 1 and Brine 2 respectively.
- As expected the EFC capital costs are significantly higher than those for EC. However, it is important to note that the capital cost calculations for EC are based on a technology that is already well established, with only relatively

marginal future equipment cost savings expected as a result of improvements in the existing technology. In contrast, EFC is a new technology with future improvements expected in the technology resulting in capital cost reductions in particular with regards to the EFC reactor.

7. REFERENCES

Buckley, C., Research into the treatment of inorganic brines and concentrates, Water Research Commission Project No. 201, Revision 1.021, May 2005.

Gartner, R.S., Genceli, F.E., Trambitas, D.O. and Witkamp, G.J., 2005. Impurity gradients in solution-grown ice and $MgSO_4.12H_2O$ crystals measured by cryo-laser ablation and high-resolution-couples plasma mass spectrograph, *Journal of Crystal Growth*, 275:1773-1778.

Loewenthal, R.E., Ekama, G.A. & Marais, G. 1989, "Mixed weak acid/base systems part 1- Mixed characterisation", *Water SA*, vol. 15, no. 1, pp. 3-24.

OLI systems Inc Stream Analyser, 2008. Version 2.0.57, OLI Systems Inc, Morris Plains, New Jersey.

Vaessen, R. (2003), Development of scraped eutectic crystallizers. PhD Thesis, Technical University of Delft.

van der Ham, F., 1999. Eutectic Freeze Crystallization, PhD Thesis, TUDelft, Netherlands