



A case study for treating a reverse osmosis brine using Eutectic Freeze Crystallization—Approaching a zero waste process

D.G. Randall*, J. Nathoo, A.E. Lewis*

Crystallization and Precipitation Research Unit, Department of Chemical Engineering, University of Cape Town, Cape Town, South Africa

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ABSTRACT

The generation of hypersaline brines emanating from industrial and mining operations poses a major environmental problem globally as the volumes of these brines increase at an exponential rate. The potential risks to the surrounding environment and water resources increase proportionally with the increased generation of these brines. The need to treat these hypersaline brines is therefore urgent.

Eutectic Freeze Crystallization (EFC) provides an alternative method for the treatment of hypersaline aqueous waste streams emanating from industrial and mining operations. The process is capable of producing potable water, as well as pure salt(s), by operating at the eutectic point with lower energy consumption than evaporative crystallization.

This paper describes a case study in which EFC was used to treat the liquid waste obtained from a Reverse Osmosis (RO) plant. The brine was obtained from a state-of-the-art plant, based on the HiPRO process, which at present converts 99% of a waste stream into potable water. The liquid waste (brine) from the plant is currently being disposed of in an evaporation pond.

In this study, a 97% conversion of the liquid waste from the RO plant was recovered as pure water, pure calcium sulphate (98.0% purity) and pure sodium sulphate (96.4% purity). The overall estimated conversion of the waste stream generated from the RO plant to viable products was calculated to be 99.9%.

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1. Introduction

One of the most important environmental issues facing many industries, especially the mining industry, is hypersaline brine production. Major methods aimed at reducing these brine volumes consist of either brine disposal in evaporation ponds, or brine treatment using evaporative crystallization. Brine disposal has a negative impact on the environment because of potential ground-water contamination, while evaporative crystallization is costly because of the high amounts of energy required. Both of these methods can reduce the volume of brine, but the final salt product is always contaminated with other salts. This makes separation of the salt waste product extremely unlikely. In addition, these current methods of brine disposal and treatment only offer short-term solutions and have not been shown to be sustainable in the long-term.

Consequently, the development and implementation of novel treatment technologies are necessary not only to produce pure water but also to produce pure salt(s), thereby alleviating the environmental burden that having to dispose of them would impose. The income generated from the sale of these salts could also be financially rewarding and be a major incentive for implementing these technologies. A recent

report from the Green Economy Initiative [1] states that the payback (health, societal and environmental benefits) for every dollar invested in water treatment is between US\$3 and US\$34.

Eutectic Freeze Crystallization (EFC) is a novel technology that has shown promise in the treatment of brines. Eutectic Freeze Crystallization is an extension of the freeze crystallization process and exploits the density differences between the ice and the salt produced to ensure effective separation. The process is operated at the eutectic point, where both ice and salt crystallize. Thus, the major problems of a mixed salt product can be avoided by the production of many pure salts at their unique crystallization temperatures.

This paper describes the results of a case study which investigated using the EFC technology to treat a brine generated from a RO plant that is currently being disposed of in an evaporation pond.

2. A case study brine

The eMalahleni Water Reclamation Plant (EWRP) was built by Anglo Coal South Africa and BHP Billiton Energy Coal South Africa (BECSA) in a partnership to address the damage done to the environment and water systems through Acid Mine Drainage in the eMalahleni area of South Africa. The state-of-the-art plant uses the Hi recovery Precipitating Reverse Osmosis (HiPRO) process technology developed by Keyplan. The HiPRO process produces 25,000 m³/d of potable water with recovery rates in excess of 99% [2]. The solid waste

* Corresponding authors. Tel.: +27 21 650 4091.

E-mail addresses: dg.randall@uct.ac.za (D.G. Randall), Alison.Lewis@uct.ac.za (A.E. Lewis).

produced from the EWRP consists of approximately 100 t/d of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and a liquid waste amounting to approximately $150 \text{ m}^3/\text{d}$ [2], which is currently being disposed of in evaporation ponds.

The solid waste is currently being treated by two processes which were developed by the Council for Scientific and Industrial Research (CSIR) South Africa to offset the high costs associated with gypsum disposal. These two processes, called GypSLiM (Gypsum processed into Sulphur, Limestone and Magnesite) and GypBump (Gypsum converted into Building and Mining Products), convert the raw gypsum into valuable products which include calcium carbonate, magnesium carbonate, sulphur as well as building and mining products. These building products are currently being investigated as an alternative material for the construction of low cost housing [2].

The disposal of the brine into evaporation ponds, which is a short-term solution in terms of dealing with the liquid waste generated from the EWRP, is not a sustainable method. At present the major focus in brine treatment is to reduce the volume of brines, a focus which usually involves evaporation ponds or evaporative crystallizers. However, these methods fail to address the negative impact that the solid products (usually in the form of mixed salts and which still needs to be disposed of) have on the environment.

3. Eutectic Freeze Crystallization

The concept of freezing a solution in order to separate water and solutes is not a new one. Many authors have described such a method as a means of separation [3–6]. Eutectic Freeze Crystallization uses these concepts and focuses on a specific area of freeze crystallization, namely operating at the eutectic point of two components (ice and salt). By so doing a number of advantages can be achieved over conventional brine treatment methods, some of which are listed below:

- The process is not complicated by the addition of added chemical compounds [7];
- From a thermodynamic perspective, as the heat of vaporisation is six times higher than the heat of fusion [8], freezing the brine as a means of treating it is theoretically less energy intensive than an evaporative process;
- Impurities are excluded from the ice structure during the crystallization of ice [9];
- The ice crystals that are produced can be used for cold heat storage [10];
- Gravitational separation of ice and salt is an added advantage during Eutectic Freeze Crystallization since at eutectic conditions both products separate as a result of their density difference. Salt sinks to the bottom of the crystallizer while ice floats to the top [11];
- Theoretically, a 100% yield can be obtained when operating at eutectic conditions [8];
- As the potential for corrosion is minimised due to the low operating temperatures [4], cheaper materials of construction can be used.

The principle of the EFC concept can be described using a typical phase diagram of a binary aqueous solution, shown in Fig. 1. The concentration of dissolved solids in waste waters is usually very low, a few grams per litre [7], thus ice will generally crystallize first because of this dilute nature. The phase diagram used to describe the EFC process therefore has the starting position on the left side of the eutectic point because this is the region where ice crystallizes first. The unsaturated solution (1) is cooled until the first crystal of A forms (2). The eutectic point is reached if the solution is cooled more. At this point both solid A and solid B are formed (3). Similarly, for a solution with a higher starting concentration than the eutectic concentration, the crystallization of salt will occur first, followed by ice at the eutectic point [11].

Previous EFC work focused on the recovery of one salt from a simple binary [8,12–14] or ternary system [15,16]. These authors

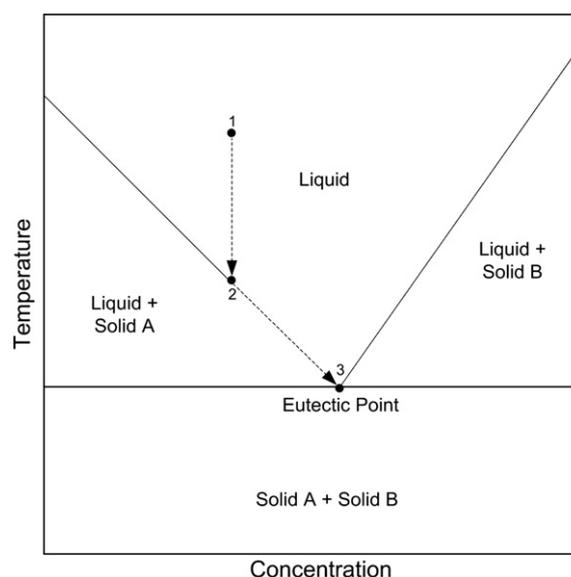


Fig. 1. Binary phase diagram showing the eutectic point.

showed the feasibility of using EFC technology for the recovery of a wide range of salts which included sodium sulphate, magnesium sulphate, potassium nitrate to name but a few. However, the applicability of using EFC to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated.

The sequential removal of individual salts from a multi-component aqueous stream using EFC technology is theoretically possible since each salt crystallizes out at its own unique eutectic temperature. Thus, multiple individual salts can be recovered in their pure form by cooling the system down to the unique eutectic temperature of each salt and sequentially removing it along with ice. The volume of the waste stream can also be significantly reduced if all the possible crystallizing salts are removed together with ice.

4. The economics of an Eutectic Freeze Crystallization process

Eutectic Freeze Crystallization has been successfully utilized for the separation of a single salt and water. However, a complete economic and technical feasibility study has not been determined for the sequential removal of salt(s) from complex hypersaline brines that are typical of reverse osmosis retentates in South Africa. Although the focus of this paper is primarily on the technical feasibility of an EFC system as applied to hypersaline brine treatment, a brief summary of the economics of the process, as applied to other systems, is also given.

Vaessen [17] investigated the use of EFC for the separation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and ice from a copper sulphate solution. The researcher determined that energy reductions of up to 70%, when compared to conventional 3-stage evaporative crystallization, were achievable for copper sulphate solutions.

A separate study involving an industrial $\text{KNO}_3\text{--HNO}_3$ solution was conducted by Van der Ham [8]. The researcher concluded that the energy costs (total costs for steam, electricity and cooling water) were significantly lower for an industrial $\text{KNO}_3\text{--HNO}_3$ solution, with a 69% reduction when compared to evaporative crystallization.

Himawan [18] conducted an economic evaluation of an EFC system for recovering magnesium sulphate and ice from an industrial waste stream. It was found that EFC could save up to 60% of the energy costs when compared to evaporative crystallization. In addition, the investment cost only increased by 7%.

Two synthetic brines, based on actual brines from the South African mining industry, were evaluated in terms of economic feasibility by Nathoo and co-workers [19]. The researchers showed

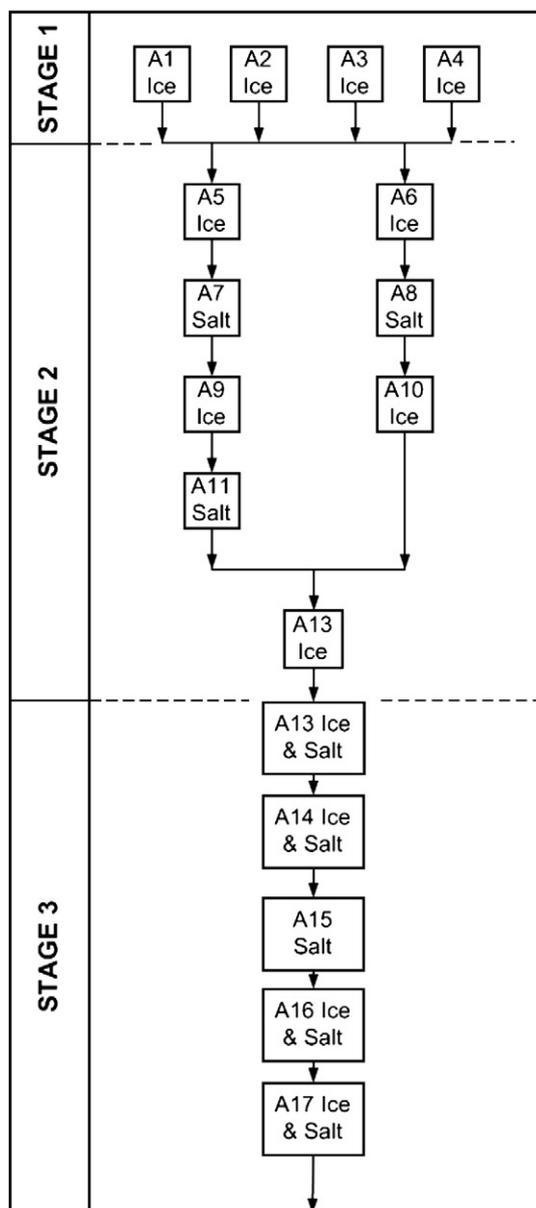


Fig. 2. Cascading concentration procedure.

that the operating cost savings of using EFC over evaporative crystallization were 80% and 85% for two Na_2SO_4 and NaCl brines of varying concentrations. Furthermore, these calculated cost savings excluded the potential income that could be generated from the sale of the pure salts produced during the EFC process, thus further strengthening the case for EFC. The capital cost for an EFC process, as compared to evaporative crystallization, was 179% to 208% higher for EFC. However, the researchers highlighted that EFC is a new process with significant room for technology improvements and thus capital cost reductions. Conversely, evaporative crystallization, as well as many other existing technologies, is already well established, with only incremental future equipment cost savings expected as a result of any further technology improvements.

In summary, the economics of an EFC process depends very much on the composition of waste water used. Substantial operating cost savings are likely to be achieved with EFC, while the capital cost for EFC, when compared to evaporative crystallization processes, is expected to be higher for EFC. As with all new technologies, the EFC capital cost is expected to decrease as the technology develops. Despite this, it is

expected that for moderate operating temperatures ($+10^\circ\text{C}$ to -10°C), the substantially lower EFC operating cost is likely to, within a short period, offset the initial higher capital cost for EFC with continued savings over evaporative crystallization and many other technologies.

5. Experimental technique

All the experiments carried out in this study to investigate using EFC as a treatment method for a multi-component, hypersaline brine were performed on an actual brine sample obtained from the EWRP.

5.1. Solution preparation

The pH of the EWRP brine was measured on site since the pH of a solution can change within 24 h [20]. The conductivity and ion analyses were conducted upon arrival at the laboratory, which usually took less than a week. The cation and anion concentrations were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

5.2. Experimental setup

The experiments were performed in a 1.5 L jacketed glass reactor. A Testo 175–177 temperature logging device was used to measure the solution temperature of the reactor. An IKA stirrer with variable speed control was used to provide adequate mixing with a 4-blade impeller. A stirrer speed of 250 rpm was used. Cooling was achieved with a Lauda RE207 thermostatic unit that continuously circulated the coolant, Kryo40, through the jacket of the reactor. The setup, excluding the thermostatic unit, was kept in a freeze room at different operating conditions depending on the stage of the cascading concentration procedure (Fig. 2).

Filtration of the final products was conducted in the cold room maintained at the same set-point temperature as the thermostatic unit. A Buchner funnel connected to a 1 L filtration flask was used to filter the ice product. A 300 mL Millipore All-Glass filter holder connected to a vacuum pump was used to filter the salt for those experiments that produced salt. The pore size of this filter paper was $0.45\ \mu\text{m}$.

5.3. Experimental procedure

Each experiment (A1 to A4 in Fig. 2) was initiated by adding approximately 1250 g of the brine that had been previously maintained at -22°C to the crystallizer. Hence the total feed to the system was 5000 g. The thermostatic unit and set-point of the freeze room were set to the same temperature and simultaneously adjusted depending on the stage of the cascading concentration procedure. These values were typically 1°C below the expected crystallizing temperature of the ice. For example, in the initial stream, ice

Table 1
Brine analysis (measured at -22°C).

Conductivity	mS/cm	22.2
pH		6.52
<i>Cations</i>		
Na^+	mg/L	6720
K^+	mg/L	1810
Ca^{2+}	mg/L	1340
Mg^{2+}	mg/L	75.00
NH_4^+	mg/L	41.50
<i>Anions</i>		
SO_4^{2-}	mg/L	16,000
Cl^-	mg/L	955.0
NO_3^-	mg/L	398
HCO_3^-	mg/L	61.2

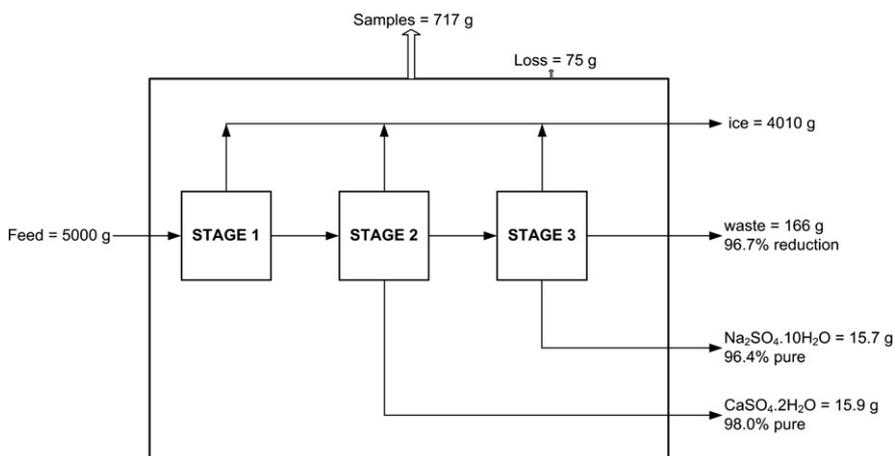


Fig. 3. Mass balance for EFC process.

crystallized at $-0.5\text{ }^{\circ}\text{C}$, thus the thermostatic unit and freeze room were set at $-1.5\text{ }^{\circ}\text{C}$. The data logging of temperature and conductivity measurements were initiated upon addition of the solution to the crystallizer. The contents of the reactor were then removed and placed in a 3 L beaker and kept in the freeze room. The ice and salt were left to stand in the beaker and allowed to separate for $\pm 10\text{ min}$ following which the ice and its entrained brine were carefully separated from the salt and its entrained brine into separate beakers. The ice was then vacuum filtered using a Buchner Funnel while the now saturated salt solution was filtered with the 300 mL Millipore setup. Finally, the ice product was washed with 50 mL de-ionised water which was pre-cooled and kept in the freeze room at the same conditions as the experiment. Liquid samples of the feed, ice (after various washes), the filtrate from the ice washing step and concentrated brine filtrate were withdrawn and analysed using ICP-MS to determine the concentration of the various cations and anions present. If salt formed during an experiment it was dissolved in de-ionised water and then sent for ICP-MS analysis.

Fig. 2 shows a cascading concentration procedure, as described by Baker [21], which was employed during these experiments. The blocks show the experiment number as well as the identity of the

solid contents obtained from each experiment. This approach was adopted because a working volume of the same concentration as that obtained from the cascading concentration procedure could not be achieved with a single 1.5 L crystallizer. Also, it was found that a solid content of more than 30% ice during the co-crystallization with salt made the separation of ice and salt extremely difficult as the entire crystallizer was filled with ice from top to bottom. Thus, to avoid this, the concentrating procedure was spread over a number of experiments.

6. Results and discussion

Upon chemical analysis, the brine was found to be rich in sodium and sulphate ions as well as potassium, calcium and chloride ions (Table 1). This is typical of the brines from the eMalahleni area of South Africa. Based on the analytical results, the brine cation–anion imbalance was less than 6%. This was deemed acceptable considering the complex nature of the water stream being investigated [22].

The concentration of sodium sulphate (anhydrous) was less than 2 wt.% which is lower than the eutectic concentration (4.2 wt.%; [23]) of a binary sodium sulphate system. This indicated that ice crystallization was expected to occur before any salt crystallization because of the dilute nature of the brine. The presence of other components can affect the eutectic temperature of either ice or salt [24] but it merely changes the temperature at which ice crystallization will occur. This was verified experimentally with ice crystallization for the feed streams (experiments A1 to A4 of Fig. 2) always occurring first. In fact, salt crystallization only occurred in experiments A7 and A8 after the stream was significantly concentrated. The concentration of the major components (in this case sodium and sulphate) can give a good indication of how dilute the brine is and whether ice or salt crystallization would be expected first.

As the exact temperature at which ice crystallization would occur was unknown, the experiments were unseeded. These unseeded experiments resulted in nucleation occurring at different temperatures because of the stochastic nature of nucleation. However, the equilibrium temperature reached after the sudden increase in temperature, due to the release of the heat of fusion, was always the same for a fixed concentration. Thus, the equilibrium temperature for experiments A1 to A4 (Fig. 2) was constant at $-0.5\text{ }^{\circ}\text{C}$. This temperature consequently defined the minimum operating temperature necessary to commence the crystallization process for that specific concentration. The other equilibrium temperatures observed for different experiments are presented in Fig. 2.

For experiments A7 and A8, the crystallization of calcium sulphate occurred after leaving the filtrates from previous experiments (A5 and A6) to stand for 24 h. This was due to the nature of calcium sulphate

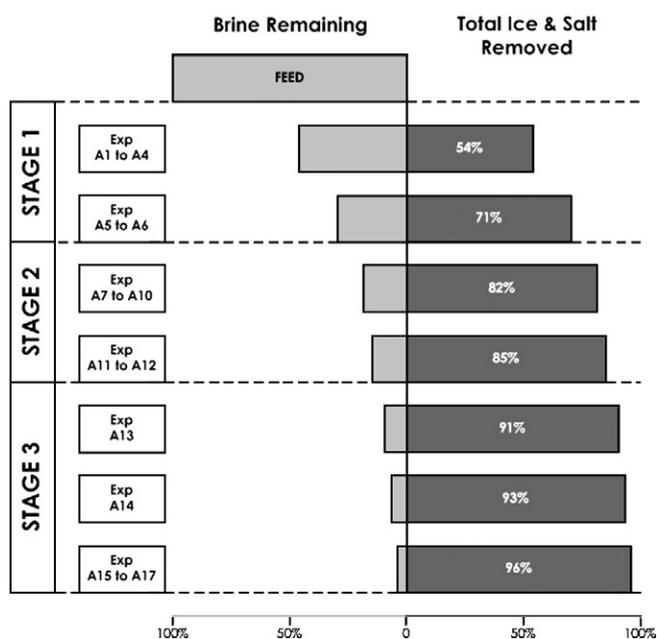


Fig. 4. Waste conversion for different steps in the cascading concentration procedure.

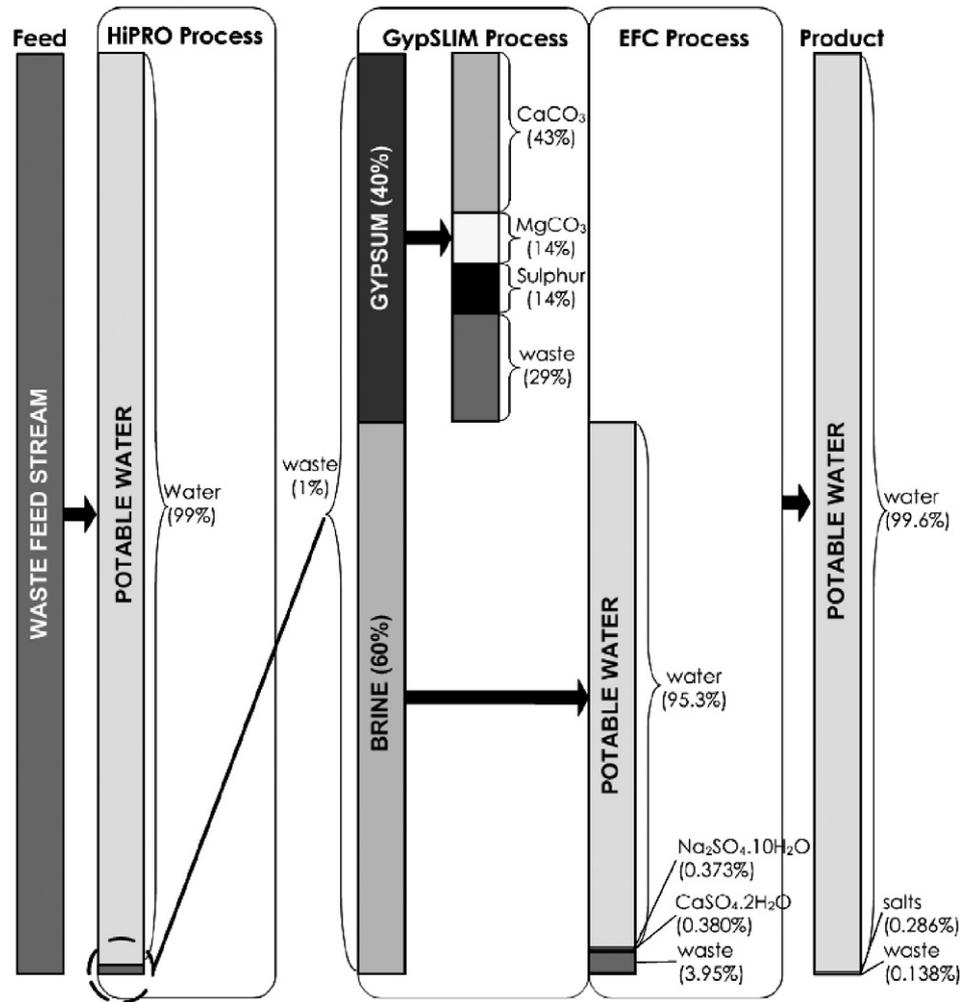


Fig. 5. Overall mass balance for a combination of treatment methods.

and its inverse solubility [25]. This was verified by leaving the filtrate obtained from experiment A9 at the laboratory temperature (22 °C) while the filtrate from experiment A10 was kept in the freeze room at 5 °C for 24 h. From this test, it was found that experiment A9 resulted in the crystallization of calcium sulphate while experiment A10 did not. Thus, the crystallization of calcium sulphate can be delayed until a lower operating temperature or it can be removed by increasing the temperature and crystallizing the salt with no ice. These approaches

provide methods of strategically manipulating the point at which calcium sulphate crystallizes out to prevent contamination.

The results obtained from the cascading concentration procedure are shown in Fig. 3. Pure calcium sulphate (98.0%) and pure sodium sulphate (96.4%) were produced along with potable water. The salt products were not washed and therefore the purity is expected to

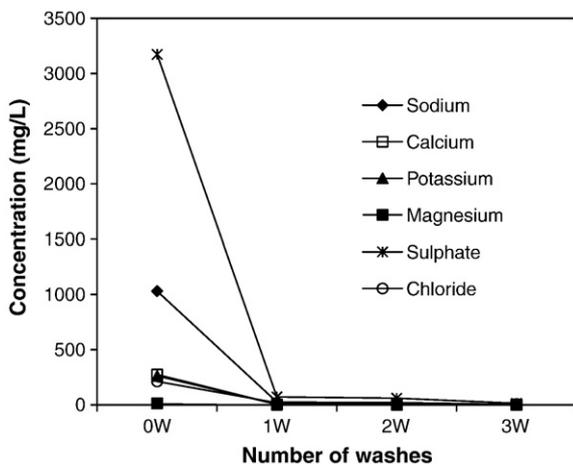


Fig. 6. Change in ion concentration for ice as a function of washes for experiment A1.

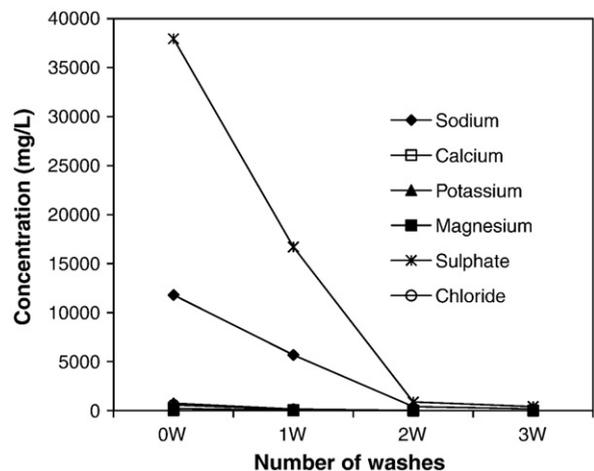


Fig. 7. Change in ion concentrations for ice as a function of washes for experiment A14.

increase with further washing. On a mass basis, a 97% reduction in the initial feed is obtained using this EFC method of treatment.

The loss calculated during the cascading concentration procedure was primarily due to the amount of liquid removed for sampling. Approximately 30 mL of solution was removed after each experiment which resulted in a loss of about 14% of the feed to sampling. Other minor losses due to evaporation and human error only attributed to about 1.5% of the experiment feed not accounted for.

Fig. 4 shows the waste conversion of the brine to viable products (water and salts) at different stages of the cascading concentration procedure. Experiments A1 to A4 resulted in the highest single conversion (54%) of the brine to ice. The overall conversion of waste for stage 1 was 71% ice since this stage was a pre-concentration stage with no salt crystallization occurring. The conversion increased marginally when salt crystallization occurred. The waste conversion for stage 2 was 85% and 96% for stage 3. There was thus a smaller increase in waste conversion from stages 2 to 3 (85% to 96%) compared to the waste conversion from stages 1 to 2 (71% to 85%).

Fig. 5 shows an overall mass balance for the treatment of waste water using different treatment methods. It includes the HiPRO process, GypSLIM process as well as the proposed EFC process. The HiPRO process, as mentioned in the Introduction, recovers 99% of potable water from the waste stream and produces a 1% waste stream. About 40% of this waste stream is solid waste that can be converted into valuable products using the GypSLIM process (Fig. 5). The remaining 60% of this waste stream can be treated using EFC.

The EFC process could in theory add a further 120 m³/d of potable water to the plant. A production of 476 kg/d CaSO₄·2H₂O and 471 kg/d Na₂SO₄·10H₂O would also be obtained. While the additional amount of water recovered using EFC may appear relatively low considering that the amount of water currently produced using the HiPRO process is 25,000 m³/d, the primary emphasis is on waste minimization and conversion of all possible waste products to useful ones (in this case calcium sulphate and sodium sulphate) rather than having to dispose of them at an additional cost. The bar on the right of Fig. 5 shows the overall conversion of the feed stream (waste) to valuable products. The product stream is 99.6% water, 0.286% pure individual salts and a 0.138% waste stream.

Fig. 5 also shows that only a combination of different technologies is capable of attaining a near zero waste discharge.

The concentration changes of the major components are shown in Fig. 6 during the crystallization of ice only (experiment A1). The limits are within acceptable South African drinking water standards after one wash [26]. These results indicate that washing can significantly reduce the entrainment of the brine with the ice crystals.

Fig. 7 shows the concentration profiles of the major components as a function of number of washes of ice obtained during ice and salt crystallizations (experiment A14). The initial concentration is much higher than that obtained during the ice crystallization alone (experiment A1). This was due to the fact that the stream was more concentrated than before and that some of the salt crystals were entrapped with the ice. Washing the ice reduced the impurity concentration levels to within acceptable drinking standards as required by the South African Department of Water Affairs and Forestry [26] after three washes.

As can be seen, novel technologies such as EFC can offer a sustainable method for the treatment of brines in accordance with the necessity for current water treatment processes to reduce the volume and extent of water pollution. There also needs to be a paradigm shift that focuses on new approaches that include wise investments and technological innovations that not only seek to obtain treated water but that also treat and convert the solid waste products into useful ones [1].

The research into using Eutectic Freeze Crystallization as treatment option for brines is still ongoing, with the current results showing promise. Work is currently underway to further reduce the volume of the brine generated from the EWRP as well as to crystallize

out more pure salt(s). The design of a pilot plant that will test the feasibility of this technology on a larger scale is also underway. The potential applicability of EFC to other brines is significant. The technology can essentially be used for any inorganic water treatment system but it would work best when used in conjunction with existing technologies such as RO.

7. Conclusion

The use of EFC as a treatment method for aqueous solutions such as brines has shown that the liquid waste obtained from the eMalahleni Water Reclamation Plant can be reduced by 97%. This would potentially take the overall water recovery to 99.9%. Pure calcium sulphate (98.0% purity) and pure sodium sulphate (96.4% purity) were also produced, along with potable water.

Novel technologies such as EFC bring the concept of a zero percent waste process closer, especially if used strategically in conjunction with existing technologies. This research is still ongoing to further reduce the waste stream of the eMalahleni Water Reclamation Plant as well as to produce more valuable salts. The design of a pilot plant using this technology is also underway.

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