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A comparative life cycle assessment of eutectic freeze crystallisation and evaporative crystallisation for the treatment of saline wastewater

M.J. Fernández-Torres *, D.G. Randall, R. Melamu, H. von Blottnitz

Chemical Engineering Department, University of Cape Town, South Africa

HIGHLIGHTS

- ► Two desalination techniques, EFC and EC, were compared by Life Cycle Assessment (LCA).
- ► EFC process is strongly preferred to EC for the modelled 4 wt.% Na_2SO_4 solution.
- ► EFC performs better for "global warming" and "non-renewable energy" impact categories.
- ► The environmental performance of EFC can be significantly reduced by heat integration.

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ABSTRACT

Two processes are compared by means of Life Cycle Assessment (LCA) to determine which one causes less environmental impact for the treatment of saline mining wastewater: Eutectic Freeze Crystallisation (EFC) or Evaporative Crystallisation (EC). EC is a well established technology whereas EFC is a new promising technology that has the potential to compete with EC but so far has not been built at industrial scale. As the processes yield by-product water in different states, system expansion was used to effect a fair comparison. The study considers three different geographical areas: South Africa, France and Europe, in order to identify the effect the source of energy has on the comparison. The energy efficiency of the chilling technology is studied parametrically. The LCA results show that for the modelled 4 wt.% sodium sulphate solution, the EFC process is strongly preferred to EC regardless of the country energy mix, requiring 6–7 times less energy resources, but also that process energy integration and chiller energy efficiency can further reduce its environmental impacts significantly.

1. Introduction

Increased water consumption is causing water scarcity problems in many countries, often exacerbated by discharges of polluted water. The mining industry is not exempt from these problems: whilst on a national scale it needs much less water than other sectors (especially agriculture or urban consumption), the local water demands and pollution potentials of a large mine relative to a small town and farming community are often considerable [1]. In response to water supply limitations, mines have increasingly started to treat and use mine water or to recover water from the tailings disposal facilities; such water is however often saline and can only be used after desalination. The resulting hyper-saline retentate poses disposal problems [2]. Evaporative crystallisation (EC) is an energy-intensive and expensive option sometimes used, producing either pure saleable salts or mixed salts to be disposed of as hazardous wastes [3].

Eutectic Freeze Crystallisation (EFC) has been proposed as an innovative technology to address these problems. Whilst EFC processes have thus far not been built at industrial scale, the technology is thought to be able to reclaim good quality water from mining wastewater whilst at the same time producing valuable products such as sodium sulphate or calcium sulphate [4]. Its energy consumption has been claimed to be significantly lower than that of alternative technology [3]. When deployed for the beneficiation of waste material, the process might thus be thought to be environmentally friendly or even 'sustainable'. Such claims of superior environmental performance should not be made without a rigorous environmental assessment.

Life Cycle Assessment (LCA) is a technique that can perform such environmental assessment since it is a "cradle-to-grave" approach. Recent case studies in which desalination technologies are compared by means of LCA include: a comparison of ion exchange and reverse osmosis [5], a comparison of reverse osmosis desalination using brackish groundwater or seawater [6], a comparison of three commercial desalination technologies (multistage flash, multi-effect evaporation and reverse osmosis) [7], a comparison of desalination technologies integrated

Abbreviations: EFC, eutectic freeze crystallisation; EC, evaporative crystallisation; LCA, life cycle assessment.

* Corresponding author at: Departamento de Ingeniería Química, University of Alicante, Apartado 99 E-03080, Spain. Tel.: +34 965903400x3012; fax: +34 965903826.
E-mail address: fernandez@ua.es (M.J. Fernández-Torres).

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with renewable energies (wind, photovoltaic and hydro-power energies) [8] and a comparison of desalination technologies with different energy production systems [9]. In these studies, the use of LCA enabled the identification of an environmentally superior technology (or feed for the same process).

This paper aims to present a comparative life cycle assessment of an EFC process and a common water treatment method used in the mining industry, namely that of EC.

2. Methods: goal and scope of the LCA

LCA is the methodology adopted in this study, as recommended by the International Standards Organization. As per the protocol in ISO 14040 [10], the goal of the study will first be stated, followed by a discussion of the scope. The document [11] has been used as a guide.

2.1. Goal

The goal of this study is to compare EFC, a technology under development, with a currently used multi-effect EC for the particular situation of separating solid salt from water. As discussed in the Introduction, this separation is becoming an increasingly used and needed step in the treatment of hyper-saline brines often associated with water circuits in the mining industry.

The two technologies have the potential to be used for the treatment of hyper-saline wastewater. In the present research, the comparison is performed on a feed brine that is made up of a single salt as the intention is to focus more on the technologies than on the behaviour of specific salts. The outcome of the comparison is primarily to be used to give direction to further technology development but also to make claims of relative environmental performance in specialist circles.

It is desirable to find out which process (EFC or EC) causes less environmental impact (quantifiably). As the material inputs and outputs will be the same in the two processes (i.e. no ancillary process chemicals are used in either process), the impact categories considered can be limited to those directly related to energy consumption only. These can be captured primarily by the indicator "depletion of non-renewable energy resources". Additionally, the indicators "global warming" and "ionizing radiation" can be used to compare emission-related impacts resulting from energy conversions. Whilst energy conversion results in a range of other impacts that are typically described by mid-point indicators such as "acidification", "eutrophication", "photochemical smog", "human toxicity" and "eco-toxicity", these are not considered here, as all of the mid-point indicators will essentially be calculated from only two major process energy requirements: electricity and heat.

The type of LCA adopted in this study is consequential, which investigates likely environmental consequences due to change in technology or processes [12,13]. The results of the study are meant to be used by:

(i) researchers in industrial wastewater treatment, especially those interested in technology innovation and in environmental sustainability research;
(ii) industrial wastewater decision makers; and
(iii) policy makers, industry, energy and environmental professionals or stakeholders, as well as implementers of wastewater treatment policies.

2.2. Scope

Two processes are considered and compared: a single EFC and an EC process consisting of three evaporative effects. The latest is an industrially frequently used arrangement. Since one of the processes is not yet industrially available, the comparison is informed by process modelling rather than by data of actual industrial performance.

The feed stream considered in the comparison represents what is called a hyper-saline wastewater in the mining industry: the intention is to completely separate water from the salts and recover both as resources. After examination of the compositions of several real multi-component industrial hyper-saline wastewaters [14] it was decided that the theoretical brine waste for this study should be simplified to one single salt which commonly appears in wastewater of the mining industry, viz. sodium sulphate. The concentration, 4 wt.%, was taken from one of the wastewaters studied in [14].

Mass and energy balance calculations were undertaken over the two process plants. The system boundary for the LCA analysis begins with the mass flowrate entry of 1000 metric ton/day hyper-saline wastewater, comprising sodium sulphate at 4 wt.%, to each process plant. The EFC process separates wastewater into salt and ice, however according to the thermodynamics of the process, the salt produced under eutectic conditions will be sodium sulphate decahydrated ($Na_2SO_4 \cdot 10H_2O$). Some of the product ice is used and melted in a heat exchanger in order to cool down the feed stream and also to save energy. The EC process separates water from the dehydrated salt and converts it into condensed steam. In order to compare both techniques by means of LCA, they need to deliver the same products.

Since anhydrous sodium sulphate is the more valuable form of the produced salt and ice is more valuable than water (from an energetic point of view), the system boundary ends when both processes produce anhydrous sodium sulphate and water in the same phase (see Fig. 1). The comparison of the two processes is achieved by the so-called "LCA system boundary expansion" [11]; in the case of EFC it will account for the production of dehydrated sodium sulphate from decahydrated sodium sulphate $Na_2SO_4 \cdot 10H_2O$, whilst the EC process will account for the production of ice from part of the liquid water (condensed steam).

2.2.1. Scenario development

Several scenarios are compared. Firstly, in the base case scenario, both processes are compared assuming that they are isolated, i.e. with no energy supply coming from other parts of the mother-plant. Since the wastewater treatment processes would generally be placed adjacent to the mother-plant, a case of energy integration is also explored. Also, the geographical context is considered in order to investigate the environmental performance of the two processes in different countries with varying energy mixes. The first setting investigated is South Africa, where mining industries have been reported to deal with hyper-saline wastewater streams [14]. As the South African energy mix is particularly carbon intensive, application of the two technologies in a country with a very different energy mix is also explored — France with its dominant nuclear electricity supply and access to natural gas for industrial heating was chosen. An average European energy mix is also explored. Finally, the efficiency of the chilling technology (reflective of its age) is varied.

2.3. Functional unit

The functional unit for the LCA investigation is the treatment of saline water to produce salt and water as shown in Fig. 1: a daily production of 40 ton of dehydrated sodium sulphate by each process and another 960 ton/day of "ice + liquid water" mixture in the amounts obtained by EFC.

2.4. Data quality

The particular EFC and EC processes considered here are hypothetical. Although there is some process data available from industrial application of EC, it was not used since i) it would be inconsistent to compare a general process (hypothetical EFC) with a specific one (real data of an EC process), and ii) in addition, there is often a

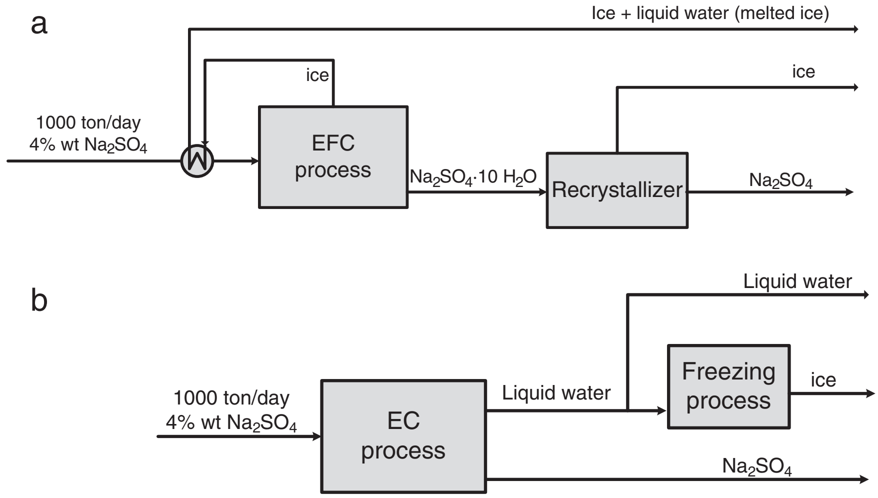

Fig. 1. Block diagrams for EFC (a) and EC (b) processes showing the boundaries for the LCA study. Both processes contain a system expansion so that the input and output products are identical.

concern with regards to obtaining authorization to publish private data from particular industries. All the thermodynamic data needed for mass and energy balances were sourced from literature [15–20].

2.5. System description

Figs. 2 and 3 represent the flowsheets of each process as considered in the present research. These flowsheet diagrams contain basic boxes representing each sub-processes, for instance, the crystallizer boxes also include the purification stage of the crystals. The flowsheet diagrams shown in Figs. 2 and 3 have been developed into these particular forms after consulting several sources of literature [18,21–23] as well as experts from the respective fields, whose contributions are acknowledged. Also, it was necessary to use a "sodium sulphate–water" phase diagram which was obtained from [16] and checked against thermodynamic data from [24]. The phase-diagram is useful since it can reveal which phases are in equilibrium at a given temperature and salt concentration.

Both processes have the same input feed stream: 1000 ton/day 4 wt.% solution of sodium sulphate in water. Fig. 2 represents the EFC process. The feed stream is first mixed with a recycle stream after which the mixture is cooled down by ice formed in the first crystallizer. Once cooled, it is fed to the first crystallizer that operates at the eutectic point. In that crystallizer three phases are present at −1.27 °C, namely: ice, decahydrated sodium sulphate and the mother liquor at the eutectic concentration. Only two streams leave that first crystallizer, ice and the decahydrated salt. For the reader's clarity, the loop of the mother liquor is shown to be exiting the crystallizer, however in a future industrial practice this stream would not be withdrawn from the crystallizer as shown here. The ice stream is taken to a heat exchanger to cool down the crystallizer feed stream causing some ice to melt. The decahydrated salt is sent to a second crystallizer where, according to the phase diagram, temperature needs to be increased beyond 32.4 °C. From this second crystallizer dehydrated salt is withdrawn as final product together with mother liquor at 33 wt.% (taken from the phase diagram) which is recycled back to the mixer.

Fig. 3 shows the detailed flowsheet diagram considered for the EC process. The feed stream is firstly mixed with a recycle stream and the mixture supplied to the first effect which operates at 48 °C. There is a closed circuit for steam/water to heat up this first effect. Some steam is produced in the first effect (Vapor 1) which will feed effect 2 as heating agent. The more concentrated liquid (Liquid 1) is further concentrated in effect 2 which operates at 40 °C. The steam produced in effect 2 (Vapor 2) is used as heating agent for effect 3. Finally, "Liquid 2" enters the third effect which operates at 33 °C, producing 3 phases: steam (Vapor 3), anhydrous sodium sulphate (one of the desired products) and saturated solution at the temperature of the third effect. The saturated solution is recycled to be mixed with the feed stream. Vapor 3 needs to condense to provide the required vacuum in the system. A barometric condenser has been suggested for this purpose. Finally, part of the water condensed from "Vapor 1 + Vapor 2 + Vapor 3" is frozen in order to obtain the same amount of ice as in the EFC case (this latest step is not shown in Fig. 3).

By looking at both flowsheet diagrams where the feed streams and the product streams are the same, one can see that the difference between the two processes, from an environmental point of view, is

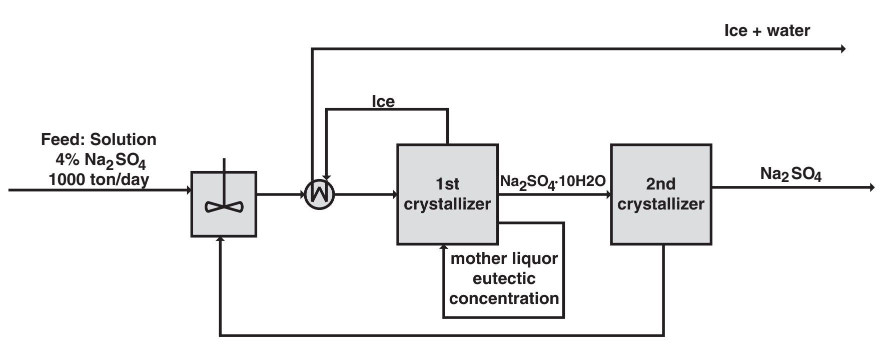

Fig. 2. Detailed flowsheet diagram considered for EFC.

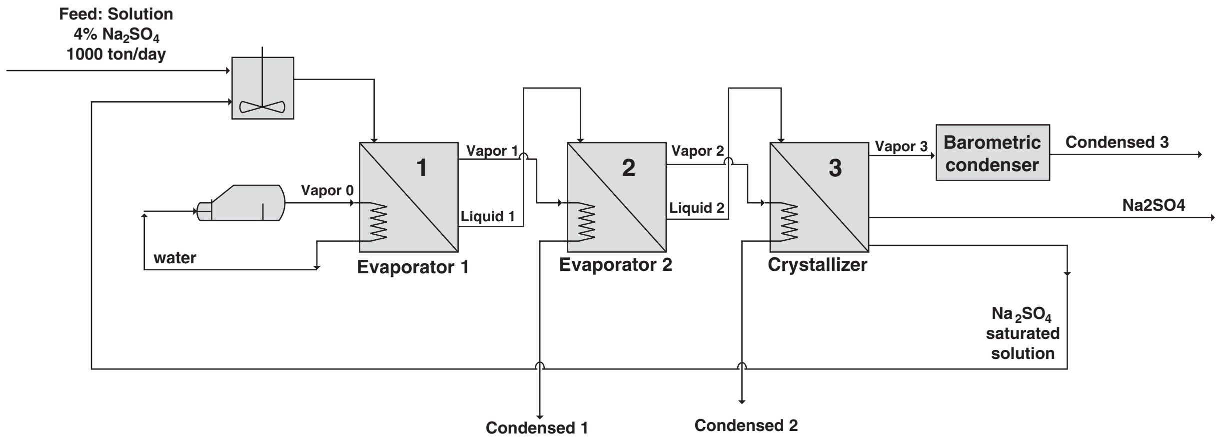

Fig. 3. Detailed flowsheet diagram considered for EC. For the sake of clarity, the freezing process to convert part of the condensed streams into ice is not shown here, but it is considered for LCA calculations.

determined by the amount and type of energy required. Therefore, the environmental impact categories considered here are those related to energy viz.: Global Warming Potential, Non-renewable Energy Use and Ionic Radiation Potential.

The impact method used for the analysis was Impact 2002+ as available in SimpaPro version 7.3 [25]. Datasets for electricity and heat generation were sourced from EcoInvent version 2.2.

3. Results and discussion

Mass and energy balances have been done to obtain the energy requirements for both processes. The mass balance for EFC has been obtained according to [26]. See the Supplementary data provided for more details on these balances. EFC requires energy in the first and second crystallizers, whereas the EC needs energy for the boiler, barometric condenser and freezing process (essential for the system expansion). The balances indicated that from the 960 ton/day of water fed to the EFC, 161 ton/day of ice melts to cool down the mixed stream going to the first crystallizer and that 799 ton/day remains frozen. Therefore, for the LCA comparison the EC process must consume additional energy to produce the same amount of ice. Similarly, the EFC process must consume extra energy to produce 40 ton/day of anhydrous salt from the decahydrated salt obtained after the first crystallizer that works at eutectic conditions.

The results of the energy analysis of the two processes can be seen in Table 1, for four different scenarios. Fig. 4 shows block diagrams representing the different scenarios described in Table 1. The thick arrows represent energy inputs. EFC and EC have been considered, firstly (scenarios 1 and 2), isolated from the mother industry, i.e., with no energy integration accounted for in the processes. The barometric condenser shown in Fig. 3 for the EC process needs cold water to operate. For scenario 2, it was specified that a closed water circuit with a chiller would be used. Once the isolated cases were studied, some considerations for energy integration were taken into account and two new scenarios were considered (Table 1):

- Scenario 3 (for EFC): the second crystallizer works at 33 °C. Many industrial processes discharge large amounts of low grade heat (by energy balance equal to the amount of high grade energy used less the change in enthalpy in process streams). In this scenario it is assumed that the energy requirement for this 2nd crystallizer could come from a different mother industry process and is therefore set to zero.
- Scenario 4 (for EC): the barometric condenser needs cold water. Assuming that there is a natural source of water close by, e.g. a river, its energy needs will not be taken into consideration.

In essence Table 1 presents an inventory of energy requirements from different sources (and of different qualities) where each one is expressed in appropriate units. In order to render these energy flows comparable, the LCA indicator “depletion of non-renewable energy resources” has been used, as discussed in Section 2.1.

The coefficient of performance (COP) of the chilling stages in all scenarios in Table 1 was taken as 4 [27], i.e. 4 J of cooling duty can be supplied for 1 J of electric energy used by the chiller. This coefficient of performance is a key technical feature of all heat pumps and continues to improve over time.

We proceeded to the 3rd part of an LCA, Life Cycle Impact Assessment (LCIA) on the basis of the results from the mass and energy balances (details in the Supplementary data). The LCIA results of the comparison of these four scenarios shown in Table 1 are presented in Fig. 5, for a South African energy mix. Fig. 5 shows the percentage of the impact as a function of each impact category considered. A 100% score means that the process under consideration has the highest environmental impact. In Fig. 5 it can be seen how EC, with no energy integration (scenario 2), performs the worst. Furthermore, EC with energy integration (scenario 4) performs worse than EFC without energy integration (scenario 1). Overall, EFC requires 6 times less non-renewable energy input than EC in the stand-alone process comparison, and 6.4 times less in the energy-integrated versions.

Since different countries obtain their energy from different sources, the geographical context was also studied by LCA. Two additional geographical locations were considered: France specifically and Europe (as an average), given that they have a higher proportion of low-carbon sources such as nuclear power, natural gas and hydro-electric generation in their energy mix.

Fig. 6 shows a comparison of the two processes for the selected impact categories considered in the France case. Scenarios considered are 3

Table 1
Energy analysis of EFC and EC for isolated processes and with energy integration. COP for all four scenarios was taken as 4.

Scenario 1: isolated EFC (no energy integration):	
1st crystallizer	2.29×10^4 kW·h/day of electrical source
2nd crystallizer	101 GJ/day from burning coal source
Scenario 2: isolated EC (no energy integration):	
Boiler	8.66×10^5 MJ/day from steam
Condenser	5.6×10^4 kW·h/day of electrical source
Ice making process	Electrical energy to freeze 799 ton/day of water
Scenario 3: EFC with energy integration:	
1st crystallizer	2.29×10^4 kW·h/day of electrical source
Scenario 4: EC with energy integration:	
Boiler	8.66×10^5 MJ/day from steam
Ice making process	Electrical energy to freeze 799 ton/day of water

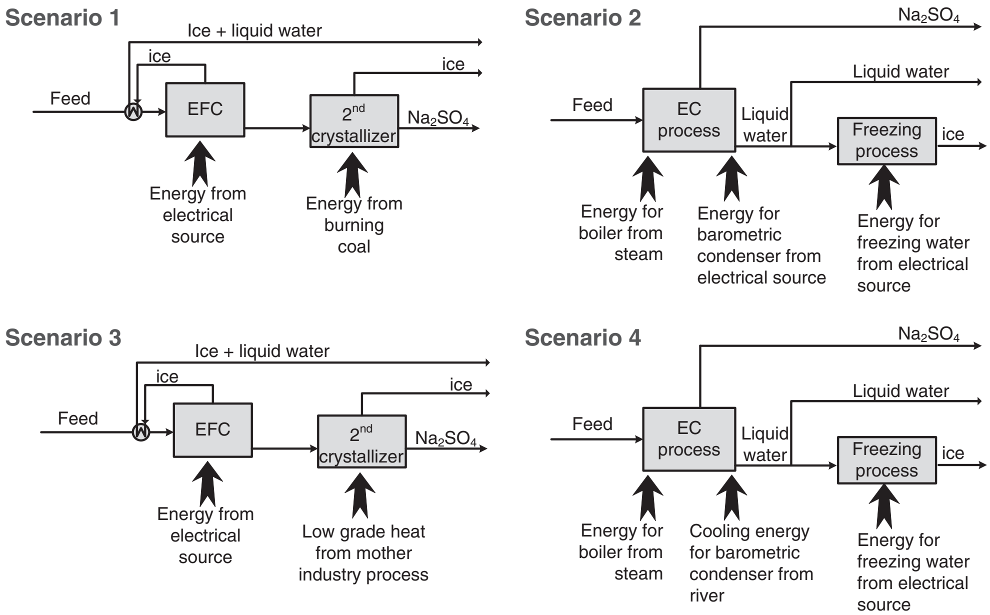

Fig. 4. Block diagrams representing the different scenarios described in Table 1. The thick arrows represent energy inputs.

and 4 from Table 1. As before, the EFC process requires 7-times less non-renewable energy, but due to the dominance of nuclear power generation for the electrical needs in this analysis, the EFC process performs 14% worse than the EC process in the impact category of "ionizing radiation".

Fig. 7 is very similar to Fig. 6, but the energy mix is the European average. Similar results to the case of France are obtained.

The relative environmental performance of EFC with heat integration for different geographical locations has been compared and the results are shown in Fig. 8. Furthermore, Fig. 8 includes the effect of varying the COP in the refrigeration cycle (first crystallizer) for the South African context only. This figure depicts up to 67% reduction in the energy use and related environmental impacts with increasing COP. The range of COP values used in Fig. 8 is taken from those obtained by [27]. The COP value assumed for the case of France and Europe is 4. Fig. 9 is included for the sake of completeness showing the results of a comparison of geographical locations for EC (where COP is 4 for all cases).

From Fig. 8 two conclusions emerge: a) an installation in France would be performing the worst in terms of "ionizing radiation", followed by installations in Europe and then South Africa. The reason for this is that France's main input of energy comes from nuclear plants, whilst Europe, on average, uses nuclear energy to a lesser extent than France but more than South Africa; b) an EFC installation in South Africa could use marginally less "non-renewable energy" than one in France or Europe (but would still have a higher "global warming" impact) if the refrigeration devices employed were of the most modern generation, i.e., with a COP of 5 or 6. The reason is that whilst both coal (dominant in South Africa) and nuclear (dominant in France) electricity use non-renewable energy, they result in vastly different CO_2 emissions which cannot be compensated by gains in end-use energy efficiency. Fig. 9 shows similar trend to that shown in Fig. 8 with similar conclusions.

4. Conclusion

The aim of the study was to carry out a comparative Life Cycle Assessment (LCA) of a Eutectic Freeze Crystallisation (EFC) process and a common water treatment method used in the mining industry, namely that of Evaporative Crystallisation (EC). Several scenarios were formulated and compared, considering various aspects, such as the effect of heat integration, type of energy supply in different geographical locations, as well energy efficiency in the ancillary refrigeration process as represented by the coefficient of performance (COP).

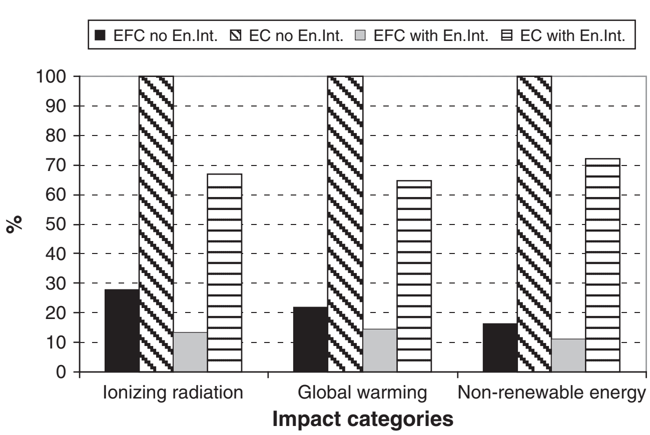

Fig. 5. LCA comparison of the four scenarios shown in Table 1 (geographical context: South Africa).

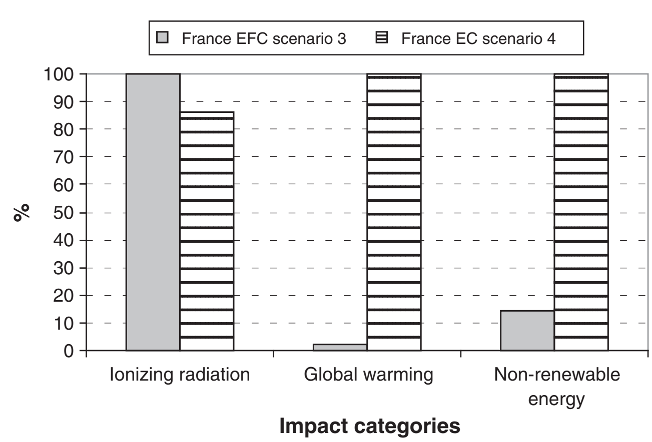

Fig. 6. LCA comparison of scenarios 3 and 4 shown in Table 1 for France.

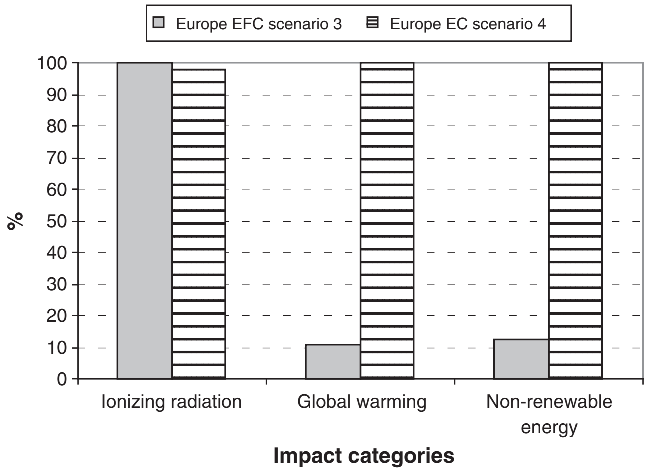

Fig. 7. LCA comparison of scenarios 3 and 4 shown in Table 1 for Europe.

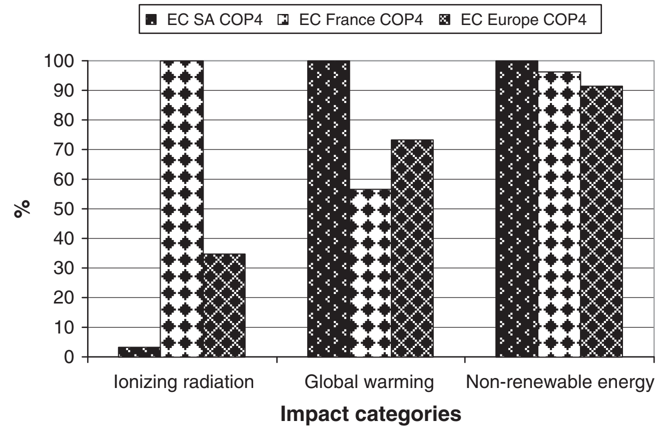

Fig. 9. LCA comparison for EC without heat integration in three different geographical contexts: South Africa (SA), Europe as average and France in particular.

Several conclusions can be withdrawn from the present work:

- According to the LCA results for the modelled 4 wt.% Na_2SO_4 solution, the EFC process is strongly preferred to EC as it uses 6–7 times less non-renewable energy to produce the same set of products.
- There is a decrease of [70–95%] for the “global warming” impact category (independent of the geographical context) when comparing EFC to EC. But the impacts of “ionizing radiation” may be 15% higher for EFC if the source of electricity used is dominated by nuclear power.
- The environmental performance of the new EFC technology can be significantly reduced by heat integration (using low grade heat from the mother-plant, and utilizing the product ice as cold utility) and by choice of efficient refrigeration technology (with high COP values).

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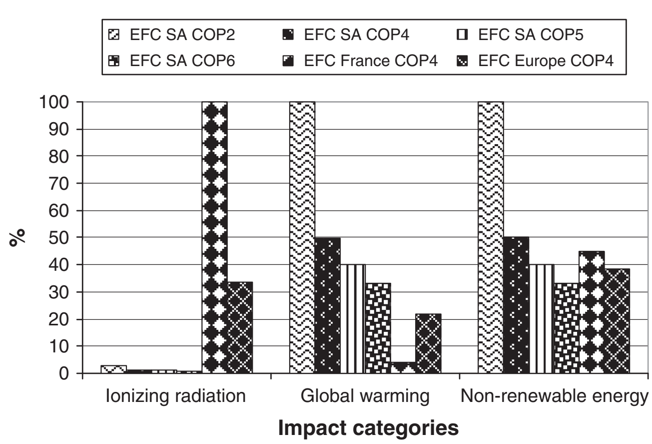

Fig. 8. LCA comparison of scenarios with heat integration in three different geographical contexts: South Africa (SA), Europe as average and France in particular. Different COP (coefficient of performance) values for the refrigeration of crystallizer-1 have been considered.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.desal.2012.08.022.

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