Eutectic freeze crystallization: Application to process streams and waste water purification

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Abstract

Two case studies are presented using eutectic freeze crystallization (EFC) as an alternative for evaporative crystallization: a 7.8 ton day^{-1} 35 w% aqueous sodium nitrate and a 24 ton day^{-1} 12 w% copper sulfate stream. The proposed crystallizer is a cooled disk column crystallizer (CDCC), using indirect cooling for heat transfer. In single stage operation, the formed ice crystals are used to pre-cool the feed stream. A two stage refrigeration unit utilizes the formed ice crystals in the condensation of refrigerant. Expressed as a thermal equivalent energy requirement, EFC requires 1282 kJ kg^{-1} NaNO$_3$ and 1037 kJ kg^{-1} CuSO$_4 \cdot$5H$_2$O. Compared to conventional multi-step evaporation, the energy reductions are 30% for sodium nitrate and 65% for copper sulfate. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Highly soluble salts are conventionally separated from their aqueous solution by evaporative or cooling crystallization. Such techniques are also frequently applied for the purification of waste water streams with a high salt content. Both techniques have several drawbacks. Evaporation of water is costly, due to the large amount of heat necessary for evaporation. In cooling crystallization, the yield is limited by the remaining solubility at low temperature. The solubility of sodium chloride for example, shows so little temperature dependency at high temperatures that evaporative crystallization is inevitable. Limitations of both techniques can be avoided by applying eutectic freeze crystallization (EFC). However, very little has been published regarding this technique. The principle of EFC can be explained from a typical water–salt phase diagram, as shown in Fig. 1. If a solution, indicated by point A, is cooled below 265 K, ice starts to form at point B. With continued cooling, more ice is formed and the solution becomes more concentrated. Its composition moves from B to C and eventually reaches point D. At this

so-called eutectic point, the solution is saturated with salt and further cooling results in the formation of pure ice and salt as separate crystals. Since the density difference between ice and a salt is typically of the order of 1000 kg m^{-3}, it is possible to separate both solids simply by gravity, as shown in Fig. 2.

A schematic representation of an EFC process is depicted in Fig. 3. The feed stream of composition A (from Fig. 1) enters the crystallizer. In the crystallizer, maintained at the eutectic temperature, heat is removed. This corresponds with the working point D in Fig. 1. The yields of ice and salt are controlled via the heat flux withdrawn from the crystallizer. The outlet of the crystallizer is connected to the solid/solid separator, where ice and salt are separated by gravity. The underflow of the separator is fed to a filter, where adhering liquid is removed from the salt crystals and recycled to the crystallizer. The top flow of the separator, containing the ice crystals, flows into a wash column. The ice is washed by a reflux stream of molten ice crystals and pure water leaves the column at the top. The wash liquor leaving at the bottom of the column is recycled to the crystallizer. With the exception of the purge streams, the feed stream can thus be separated into pure water and salt.

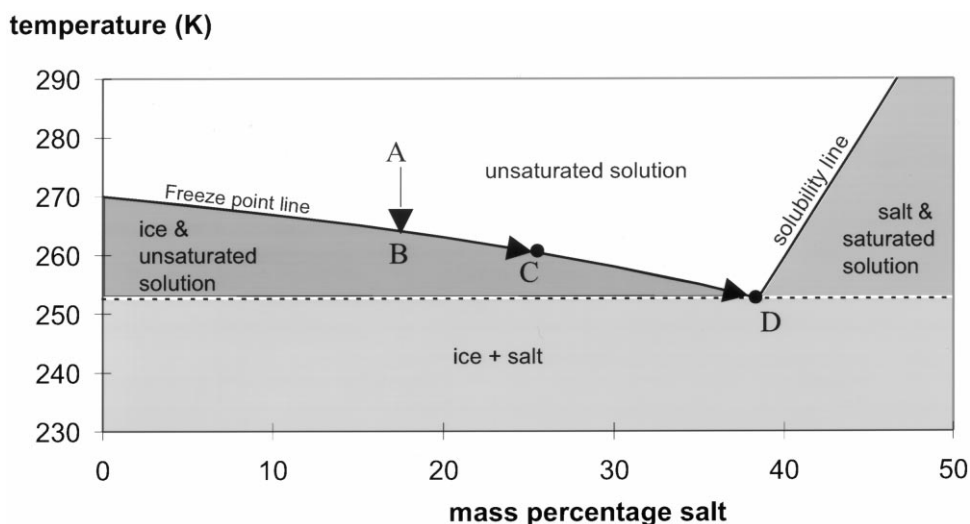* Corresponding author. Tel.: +31 15 2786605; fax: +31 15 2786975; e-mail: F.vanderHam@wbmt.tudelft.nl

Fig. 1. A water–salt phase diagram; point D is the working point of EFC.

The aim of this work is to propose a design for an EFC process for two cases and to compare its operation with that of conventional evaporative and cooling crystallization.

2. State of the art of the EFC process

Freezing technology became of interest in the late fifties for application in water purification. Although its potential was investigated thoroughly, its actual implementation for sea water desalination was never implemented on large scale [1]. In other fields of application however, such as the food industry, freeze concentration is now commonly used [2]. NIRO (formerly Grenco) has developed a freeze concentration (FC) system that is commercially used in the food industry and recently also in waste water management [3]. These concentration processes are, however, different from the EFC process, where two solids are formed simultaneously. Little information has been published on the subject of EFC, presumably due to the alleged complexity of EFC compared to competitive conventional techniques, such as evaporative and cooling crystallization. With the ongoing advancements in wash column technology and the large scale application of melt crystallization as an ultra purification technique, the most prominent disadvantages of EFC concerning investment costs and scale limitations can be overcome. In time therefore, it has come to be considered for commercial application.

EFC involves the creation of two solids and the major concern is expected to be the control of the shape and size distribution of the ice crystals that have to be fed to the wash column. Formation of ice crystals from aqueous solutions can be achieved by either direct or indirect cooling. In the case of direct cooling, an inert cooling fluid is injected into the solution and vaporizes at the desired temperature. Its heat of evaporation is withdrawn from the solution, which causes cooling of the solution. EFC based on this principle has been reported by Stepakoff et al. [4]. An important drawback with this method of operation is that the cooling fluid is more or less present in all equipment: solid/solid separator, filters, wash column, pumps, etc. as reported by Stepakoff et al. [4]. The second and more common principle is indirect cooling, where the cooling liquid is not mixed with the solution, but flows through pipes or jackets. The total surface area that is needed for cooling is the key parameter here, as well as the heat transfer coefficient.

With indirect cooling, two options are available for the formation of ice crystals from aqueous solutions: nucleation/ripening and suspension cooling. The nucleation/ripening principle is used in the previously mentioned NIRO process and works as follows: in a scraped heat exchanger, small ice nuclei are formed. These small ice crystals are transported to a large ripening tank and maintained at constant temperature. Here, small crystals dissolve and large crystals grow. It is expected however, that the two solids formed in the scraped heat exchanger will be impure due to their very fast (and therefore uncontrolled) growth. In this EFC study, slow suspension cooling is pursued, where nucleation and crystal growth of both solids are combined in one (large) vessel. A column type crystallizer that should serve this purpose, is proposed in Fig. 4.

The feed stream is introduced in a cooling disk column crystallizer (CDCC), maintained at the eutectic temperature. Heat is removed through cooled disks mounted on an axis in the column, which are analogous to the rotating disk contactor used in extraction. The
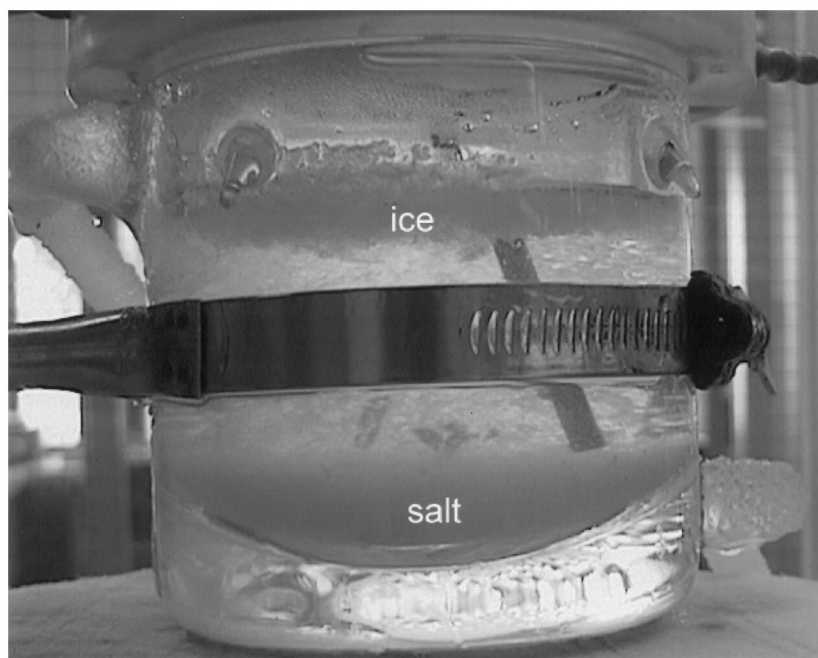
Fig. 2. Photograph taken of a 200 ml vessel operating EFC; after the stirrer is turned off, ice floats to the top of the vessel and salt to the bottom.
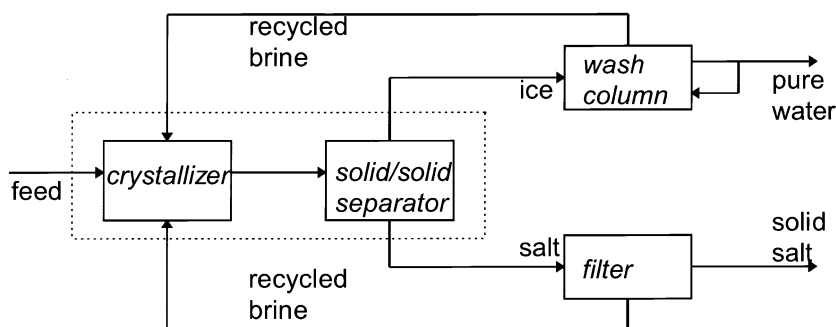

Fig. 3. Schematic representation of the EFC process for the production of pure water and salt from waste or process streams.

disks have orifices, allowing the crystals to move between compartments. To avoid scaling on the disks, they are equipped with scrapers, wiping the disks clean and providing mixing within the compartments. Due to the large density difference of ice and salt crystals, the ice crystals are expected to float to the top of the column while the salt crystals sink to the bottom. In this way, separation of the solids is achieved along their formation.

3. EFC energy requirements and design aspects

3.1. Recovery of heat

Recovery of heat in the EFC process can be achieved in two ways, as shown schematically in Fig. 5. In option A the ice crystals are melted and the heat liberated at 273 K is used to cool the feed directly to 278 K. In option B, the ice is used in a two stage refrigeration unit. In this two stage ammonia cycle, the melting heat of the ice crystals is used to condense part of the ammonia to 278 K in condenser 1. The remaining ammonia vapor is condensed in condenser 2 using cooling water at 303 K, as in the single stage unit A. The condensation pressure of ammonia at 278 K (5.1 bar) is about half the pressure at 303 K (11.5 bar), therefore the compressor duty is considerably reduced. The amount of ice available determines the fraction of the ammonia that can be condensed in condenser 1 and therefore the reduction in compressor duty. Define $\varsigma = \Phi_{Cond1}/\Phi_H =$ (condenser 1 duty)/(desired cooling capacity). The overall performance of the refrigeration unit will be higher for a two stage unit if the amount of ammonia going to the first compressor is high compared to the amount going to the second compressor, i.e. the performance increases with increasing ς. The coefficient of performance (COP) is defined as COP = Φ_H/Φ_W, with $\Phi_H =$ desired cooling capacity in Watts and $\Phi_W =$ work (electric power consumption) in Watts.
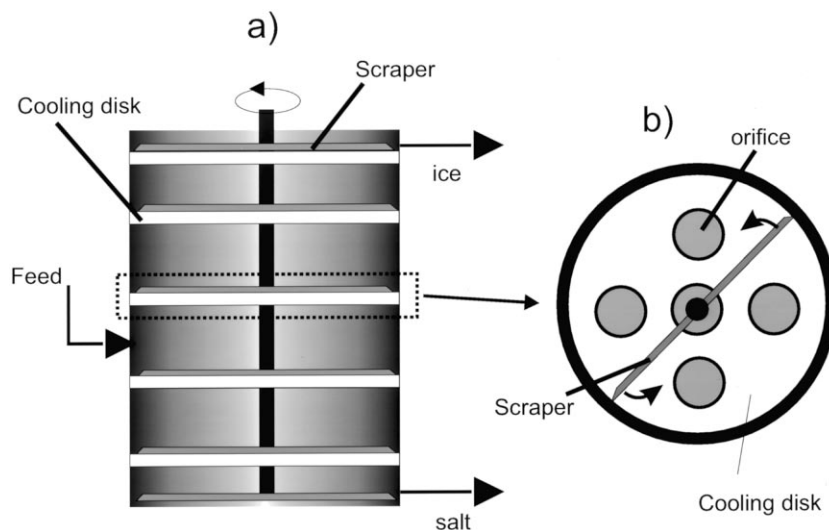
Fig. 4. Proposed crystallizer type. CDCC: (a) side view, (b) top view. Ice is formed on the cooling disks and scraped off by the scraper; gravity transports the ice through the orifices to the top of the column, while salt (which is mainly formed in the bulk) sinks to the bottom of the column.

For different operating temperatures, the COP of a two stage refrigeration unit is plotted as a function of ς in Fig. 6. ASPEN 9.1-3 was used to calculate these values. To use Fig. 6 for a given aqueous stream, first multiply the flow rate of water in the stream by the melting heat of ice (334 kJ kg^{-1}) to get Φ_{Cond1}; this value must be divided by the desired cooling capacity in Watts to get ς. From Fig. 6, the overall COP can now be deduced. The electrical power consumption of the process can then be calculated by dividing the cooling capacity by the COP.

Notice that ς increases with decreasing concentration. A low concentrated feed stream can therefore still be economically processed using EFC. For small scale operations, a two stage unit would not be feasible, due to higher investment costs.

3.2. Case study I: EFC application to 7.8 ton day^{-1} waste stream of NaNO$_3$

A new production process gives rise to a discharge of 7.8 ton day^{-1} aqueous solution of sodium nitrate, unless the salt can be recovered from the dilute solution. Recovery of this sodium nitrate is desirable for environmental reasons, but it would also improve the efficiency of the process, since the sodium nitrate can be recycled to the plant. The conventional technique would be evaporative crystallization, but the sodium nitrate solubility is very high at high temperatures, resulting in a viscous mixture that is hard to crystallize by evaporation. Operation under very low pressure or granulation could be a solution, but on a small scale plant of 7.8 ton day^{-1}, this is not feasible. The sodium nitrate content is 35 w%. Membrane techniques such as reverse osmosis and electrodialysis are not possible at

such a high concentration and do not produce solid sodium nitrate. A feasibility study was performed for EFC operation based on a CDCC column.

The eutectic temperature of the system sodium nitrate–water is 255 K. For single stage refrigeration (option A in Fig. 5), the feed is cooled from 298 to 278 K by melting product ice. The remaining cooling requirements for the CDCC are: (1) cooling the feed from 278 K to the eutectic temperature (255 K); and (2) formation of ice and solid sodium nitrate. These energy requirements are presented in Table 1 and add up to 35.5 kW. The required cooling in two stage operation equals 43.0 kW. This higher energy input compared to single stage is due to the fact that the feed must be cooled from 298 to 255 K, instead of from 278 to 255 K in single stage operation.

The electrical power consumption of the refrigeration unit depends on the amount of heat that must be removed and the temperature at which this energy is removed. The disks of the CDCC are cooled using an electrolyte solution as a coolant. The coolant is pumped through a shell-and-tube type heat exchanger cooled by the refrigeration unit. The temperature difference between the cooling disks and the CDCC contents is the driving force for crystallization and cannot be too large, in order to prevent scale formation on the cooling disks and poor crystal shape and/or size. However, it cannot be too small, since a very large CDCC cooling area must be avoided. The temperatures of the coolant entering and leaving the CDCC are taken as 249 and 253 K, respectively. The average temperature difference between disks and bulk fluid is therefore 4 K. The shell-and-tube heat exchanger from where the cooling liquid is pumped is thus maintained at 249 K by the refrigeration unit. The refrigeration temperature is set 4
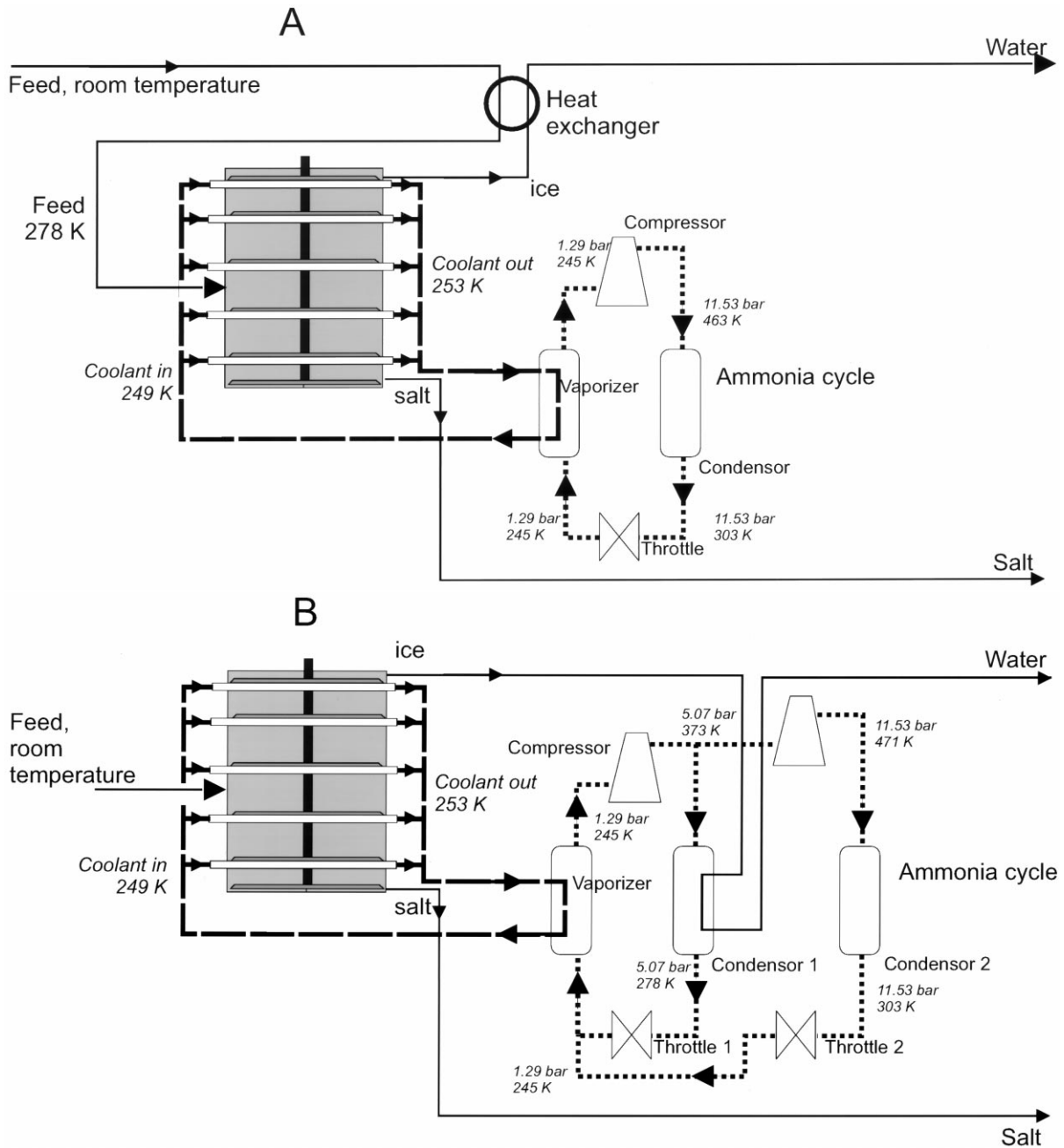
Fig. 5. Heat recovery in EFC by means of: (A) exchange of heat between the feed at room temperature and the formed ice. In this way, the feed can be cooled to 278 K; and (B) a two step refrigeration unit. The first condenser is operated at 278 K. The formed ice is used as a condensing medium. The remaining heat is withdrawn in condenser 2. The performance of this two step unit is better than that of a single step refrigeration unit, especially at relatively high eutectic temperatures.

K below the shell-and-tube exchanger and equals 245 K for both single and two stage units (options A and B in Fig. 5).

The COP of the single stage unit can be deduced from Fig. 6 at $\zeta = 0$, i.e. COP = 2.43. The electrical power consumption is therefore 35.5/2.43 = 14.6 kW. For the two stage refrigeration unit, $\zeta = 0.45$, corresponding to COP = 2.79 (Fig. 5). The electrical power consumption is therefore 43.0/2.79 = 15.4 kW. The re-

sults are summarized in Table 2. The energy requirement is higher for two stage operation than for single stage. This is because the increase in COP of the two stage unit, from 2.43 single stage to 2.79 in two stage, is small compared to the increase in the required cooling duty for two stage operation (from 35.5 to 43.0 kW). It is important to note that the concentration of the feed stream is a significant factor in choosing between single and two stage refrigeration. For less concentrated feed
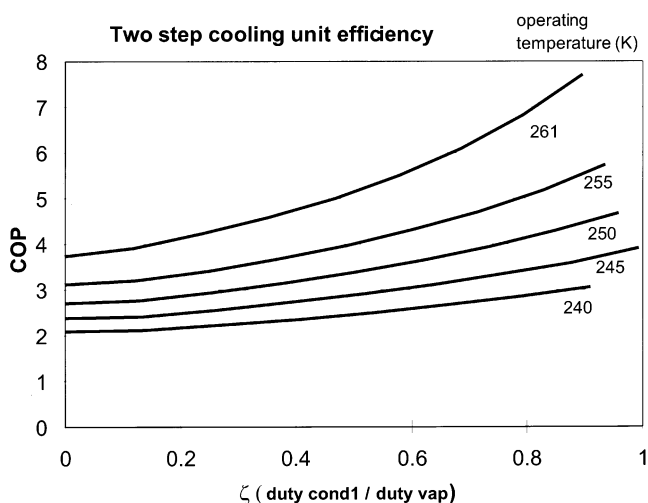
Fig. 6. Overall COP of a two stage refrigeration unit versus the ratio of the condenser duty available at 278 K to the vaporizer duty required; the different lines correspond to different vaporizer temperatures. For a single stage unit $\varsigma = 0$.

streams, the latter option is more favorable because the inevitably larger amount of ice produced leads to an increase in both ς and COP.

For a fair comparison between thermal (necessary for evaporative crystallization) and electrical (EFC) energy requirement, conversion from electrical to thermal energy is achieved by multiplying the electrical energy requirement by three. For single stage operation, the energy requirement is 31% less than that for evaporative crystallization, while for two stage operation the requirement is 27% less than that for evaporative crystallization (see also Table 3).

3.3. Case study II: EFC application to a 1 ton h^{-1} process stream of $CuSO_4$

As in the previous case, calculations were carried out for a 1 ton h^{-1} 12 w% $CuSO_4$ solution. The eutectic temperature of the system $CuSO_4$–water is relatively high (271 K). At this temperature, $CuSO_4 \cdot 5H_2O$ is formed. The temperature in the vaporizer is set to 261 K. For single stage operation, the electrical power consumption is 22.8 kW, whereas two stage operation requires 17.9 kW. In contrast to case I, two stage operation requires less energy than single stage (see also Table 1 and Table 2). The energy requirement is compared with conventional three step evaporation. The same conversion factor of three is used to 'convert' electrical energy to thermal. Compared to evaporative crystallization, the energy reduction for single stage would be 62% and for two stage, 70% (see also Table 3). Compared to single stage evaporative crystallization, the energy gain would be much higher.

4. Discussion and conclusions

Compared to conventional three stage evaporative crystallization, EFC requires less energy per kg product. Energy reductions up to 70% can be achieved. The 100% conversion into water and salt is an advantage when compared with cooling crystallization.

An EFC process with a two stage refrigeration unit does not necessarily consume less energy than one with

Table 1
EFC cooling requirements for both cases

	Cooling feed (kW)	Ice formation (kW)	Salt formation (kW)	Total (kW)
$NaNO_3$				
Single stage	8.5	19.4	7.6	35.5
Two stage	16.0	19.4	7.6	43.0
$CuSO_4$				
Single stage	7.7	75.5	2.5	85.7
Two stage	31.0	75.5	2.5	109.0

Table 2
Power requirements for the two case studies

Operation	Cooling required (kW)	ς	COP overall	Electrical power consumption (kW)
$NaNO_3$				
Single stage	35.5	0	2.43	14.6
Two stage	43.0	0.45	2.79	15.4
$CuSO_4$				
Single stage	85.7	0	3.75	22.8
Two stage	109.0	0.69	6.10	17.9

Table 3
Comparison of energy requirements between EFC and conventional evaporation; Conversion between electrical and thermal energy is done by multiplying the electrical energy by three

	Cooling duty Q electric (kW)	Equivalent Q heat (kW)	Requirement (kJ kg^{-1} salt)	Reduction compared to evaporation (%)
NaNO$_3$				
Single stage	14.6	43.8	1382	31
Two stage	15.4	46.2	1459	27
Two step evaporation			2000	
CuSO$_4$				
Single stage	22.8	68.5	1326	62
Two stage	17.9	53.6	1037	70
Three step evaporation			3485	

a single stage unit. For the sodium nitrate case, the increase of the COP for a two stage refrigeration does not compete with the increase in cooling duty required, as can be seen in Table 2. If the feed stream were less concentrated however, more water would be available and a two stage refrigeration would require less power than single stage.

EFC can potentially be applied to various process or waste streams. The calculations presented here are based on realistic assumptions for the driving forces needed for crystallization and heat transfer. The two cases presented in this work have eutectic temperatures between 255 and 271 K and it is a reasonable assumption that every system with a eutectic temperature between these two values can be feasibly pro-cessed with EFC requiring less energy than evaporative crystallization. In the near future, experimental evaluation will be performed using the pro-posed CDCC crystallizer with an industrially relevant system.

Appendix A. List of symbols

ς	ratio of condenser 1 duty by desired cooling capacity
Φ_{Cond1}	duty condenser 1 (kW)
Φ_H	desired cooling capacity (kW)
Φ_W	electrical power consumption (kW)

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