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Teaching a new technology, eutectic freeze crystallization, by means of a solved problem

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ABSTRACT

A solved design problem of how to deal quantitatively with crystallization problems below the eutectic temperature is presented. This problem serves as an excellent pedagogic complement to undergraduate students of chemical engineering since it is solved by means of a solubility diagram. It also promises novelty and environmental improvement to students, exposing them to eutectic freeze crystallization (EFC) technology, which is gaining momentum to be implemented in waste water treatment. By means of mass balances together with the solubility diagram, the proposed problem involving two crystallizers and a recycle stream is solved, and in so doing teaches students about the possible application of EFC in the treatment of brines.

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Keywords: Pedagogic problem; Eutectic freeze crystallization solved problem; New technology

1. Introduction

Crystallization is a unit operation that is generally not deeply treated in the Chemical Engineering undergraduate curriculum. Other unit operations, such as distillation or gas absorption, are traditionally studied to a greater extent and in far more depth. This fact is also obvious from the number of pages dedicated to different unit operations in chemical engineering textbooks such as Coulson and Richardson (1978), Foust et al. (1980) or McCabe et al. (2001).

An interesting aspect of crystallization with respect to the chemical engineering undergraduate curriculum is that it requires an ability to understand and interpret solid–liquid phase diagrams. A useful pedagogic variation for undergraduates would be to learn how to quantitatively solve crystallization problems by means of solubility diagrams. There are very simple diagrams with a unique eutectic point and only two solid phases. But there are also very complicated diagrams with a number of eutectic points and different solid phases (hydrates). See for instance Fig. 22 (for naphthalene in benzene) and Fig. 23 (for ferric chloride in water) of Hougen et al. (1954).

Many books can be used to learn the basics of solid–liquid phase diagrams (e.g., Felder and Rousseau, 1986[1]; Foust et al., 1980; Hougen et al., 1954). A brief summary of the theory is presented in the *background* section of this paper (Section 2.2). Despite the depth with which these books treat crystallization phenomena, none of them show how to deal specifically with situations where the working temperature is below the eutectic point. This is particularly interesting with regard to the novel technique of eutectic freeze crystallization (EFC) which has been gaining momentum to be implemented as a waste water treatment process.

The objectives of this paper are, on the one hand, to present the characteristics of solubility diagrams and how can they be used to make predictions once equilibrium has been reached in a crystallization process. In particular, it will be illustrated how to deal with mass balances for a system containing a crystallizer operating below the eutectic temperature. As an example, sodium sulphate in water has been chosen to serve

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[1] There is a new edition of Felder and Rousseau, but the latest does not include a solid liquid equilibrium section in chapter 4.

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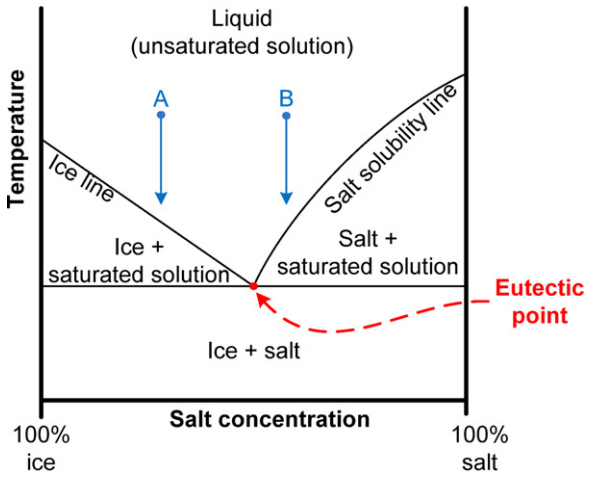

Fig. 1 – Schematic representation of the simplest solid–liquid phase diagram at constant pressure.

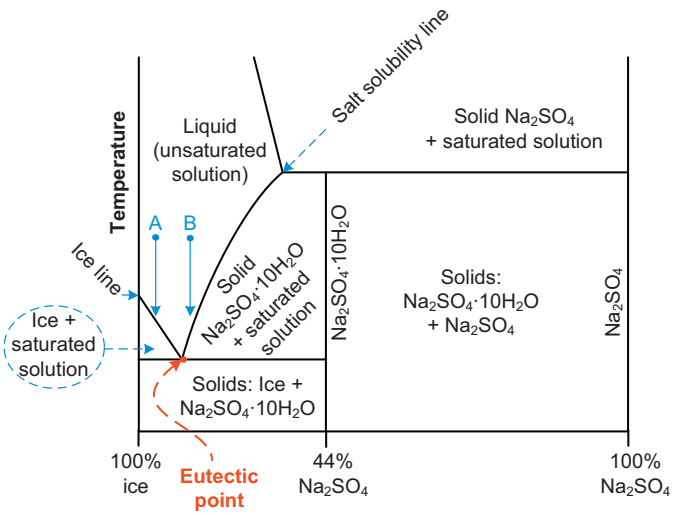

Fig. 2 – Schematic representation of the sodium sulphate/water solid–liquid phase diagram (after Hougen et al., 1954).

as the system. On the other hand, this paper aims to show the possible application of EFC in the treatment of brines. With these objectives in mind, a pedagogic design problem focusing on the mass balance of an EFC process for the crystallization of sodium sulphate is posed and solved. Others have also published solved problems because many academics and students of chemical engineering find them very useful (Foley, 2011; Thibault et al., 2010).

2. Background

Solid–liquid phase diagrams and EFC will be briefly introduced before the problem is posed and solved.

2.1. *Solid–liquid phase diagrams*

A brief explanation of simple phase diagrams such as the one shown in Fig. 1 is as follows: the diagram plots temperature vs. salt concentration for a water–salt system. Depending on the temperature and concentration, different phases will be present. The left vertical axis represents 100% ice, whereas the right vertical axis represents 100% salt. The figure exhibits different areas: "liquid (unsaturated solution)", "ice + saturated solution", "salt + saturated solution", "ice + salt", all separated by "equilibrium lines". In those areas, the solid phase present is indicated. The "eutectic point" (at which the mixture has its lowest freezing point) is indicated in red. The equilibrium lines plotted in any phase diagram are *equilibrium* data, i.e., they are made up of an infinite number of points (mass fraction, temperature) at which *equilibrium* has been reached between the solid phase and the saturated solution. In practice, those lines can be crossed without the appearance of any solid as long as equilibrium has not been reached. In such situations a *metastable supersaturated solution* is obtained. If crystallization nuclei are added, crystallization will take place and the solution concentration and temperature will return to their equilibrium values (on the equilibrium line). The existence of these metastable supersaturated solutions will be ignored in this paper where it will be assumed that a state of equilibrium is maintained at all times.

If a liquid solution with concentration and temperature as that depicted by "A" in Fig. 1 is cooled down (vertical displacement, blue arrow), it will remain at the same concentration until the blue arrow touches the "ice line". At that point, a small portion of ice will appear. Similarly, if a liquid solution such as "B" in Fig. 1 is cooled down, it will remain at the same concentration until the blue arrow touches the "salt solubility line". Then, a small amount of salt will appear. Inside any of the blocks representing solid phases ("ice + saturated solution", "salt + saturated solution", "ice + salt") the very familiar lever rule can be applied.

A brief explanation of more complicated phase diagrams such as the one shown in Fig. 2 is as follows: the diagram again plots temperature vs. salt concentration for the particular case under consideration in this paper, sodium sulphate/water. The left side of this figure (from 0% of Na_2SO_4 till 44%) can be used exactly as that of Fig. 1. The value of 44% represents the concentration of pure Na_2SO_4 in the hydrate $Na_2SO_4 \cdot 10H_2O$, i.e. (MW of Na_2SO_4)/(MW of $Na_2SO_4 \cdot 10H_2O$) = 0.44 where MW stands for molecular weight. The other two new areas ("solid Na_2SO_4 + saturated solution" and "solids Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$") are again areas where two phases coexist and the lever rule applies.

2.2. *Eutectic freeze crystallization (EFC)*

Mining processes make use of large quantities of water that in part ends up as waste water (usually made up of brines). For environmental and economical reasons this water should be thought of not as waste, but as a source of water and minerals. A number of techniques can be employed to separate the water and the minerals. For instance, there are various water recycling technologies that mines could consider (or that are already in use) to minimize their fresh water consumption, including inorganic precipitation, ion exchange and membrane treatments. As a consequence, most of these treatment methods produce concentrated amounts of inorganic brines. To treat these brines many management strategies have been used (Jivanji, 2011): evaporative crystallization, solar evaporation, wind aided intensified evaporation, dew-vaporation, extractive crystallization, ion exchange resins, freeze crystallization and EFC.

EFC is a new technology that could provide an innovative solution to treating brines and concentrates, producing purified water and high purity salts (Jivanji, 2011; Lewis et al., 2010; Reddy et al., 2010; Rodriguez-Pascual et al., 2010). At the

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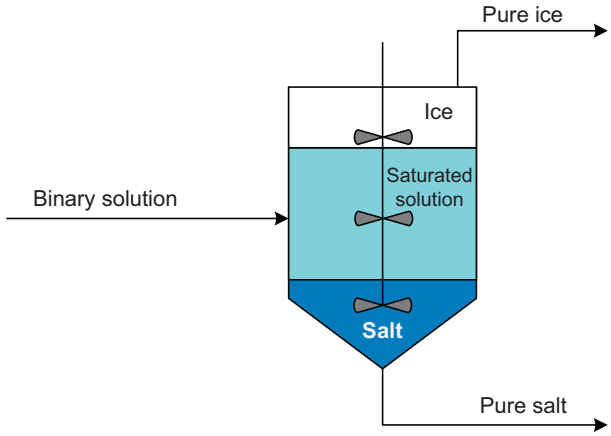

Fig. 3 – Simplified representation of the functioning of a eutectic freeze crystallizer.

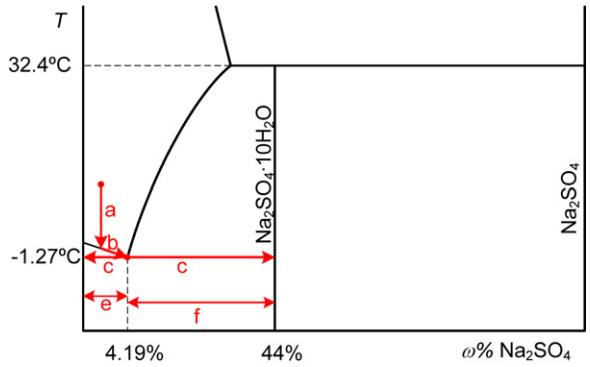

Fig. 4 – Na_2SO_4–water equilibrium phase diagram, not to scale (after Hougen et al., 1954). The red line indicates the path followed by the feed stream in the first crystallizer.

eutectic point of a binary system, three phases coexist: ice, salt and saturated solution. By cooling down the brine to the eutectic point temperature, ice and salt will crystallize out. These two solid phases can be easily separated, due to their differences in density, i.e., ice will float on top of the saturated solution, while the salt will sink to the bottom of the crystallizer. Fig. 3 shows schematically and in a simplified manner how such a continuous eutectic freeze crystallizer might operate for a binary solution. It is appropriate to mention here that EFC could also be applied to waste water containing multiple ions, requiring for that situation, several eutectic freeze crystallizers arranged in a sequential manner (Jivanji, 2011), but this topic is outside the scope of this paper.

It is worth noting that the separation shown in Fig. 3 is a simplification of the real process. The salt–ice separation has some problems of agglomeration and aggregation because of the ice morphology; therefore, two extra separators are always required (Vaessen et al., 2003; Van Spronsen et al., 2009): one where the ice is washed with recycled pure water and another where the salt is washed with saturated solution.

For the best performance in the eutectic freeze crystallizer, it is recommended by Himawan et al. (2006) that the amount of solids inside the crystallizer be below 20% for continuous operation during crystallization of $MgSO_4{\cdot}7H_2O$ in a scraped wall crystallizer (SWC) and up to a maximum of 40% in batch mode. These operational values are highly dependent on the crystallizer design and the crystals' characteristics, esp. their morphology, growth rate and density.

3. EFC problem statement and solution

The statement of the problem follows: design a plant to separate Na_2SO_4 from water by means of EFC. The salt product at the eutectic point is decahydrated but we need to produce it in anhydrous form, therefore a second crystallizer will be necessary at this plant. For the best performance of the first crystallizer, it is recommended that the amount of solids inside the crystallizer be maintained at 30%. Feed information follows: 100 Tm/day of solution at 4 wt.% Na_2SO_4 and 15 °C. For environmental and economic reasons, only two streams should leave the plant, 4 Tm/day of anhydrous Na_2SO_4 and 96 Tm/day of water, therefore any other stream leaving the crystallizers should be recycled back. The student could be given, or not, thermodynamic information with which to solve the mass and energy balance more readily. If decided to be given, this information could be taken, for example, from Fig. 19.28 in Foust et al. (1980) and Fig. 24 in Hougen et al. (1954).

Simplifications: depending on the design problem scope and associated learning outcomes, the system can be thought to achieve perfect solid-liquid separations after each crystallizer, and metastability can be ignored.

3.1. *Solution*

For the resolution of this problem the students would have to know beforehand how to work with phase diagrams. If they have not covered this material during their undergraduate studies, they can be referred to the books mentioned in the introductory section of this paper.

For the system under study (Na_2SO_4–water) the eutectic point is found at 4.19 wt.% concentration of Na_2SO_4 and at a temperature of −1.27 °C (see Fig. 4). The phases in equilibrium at the eutectic point are ice, mother liquor at the eutectic concentration and $Na_2SO_4{\cdot}10H_2O$ which constitute the output streams of the first crystallizer operating at the eutectic point (see Fig. 4 for path details).

Fig. 4 shows in red what would be the path of the feed stream inside the first crystallizer. At first the feed stream will get colder (straight vertical path a) until the temperature reaches the solid–liquid equilibrium line "ice line". Then, from that point down to the eutectic point (path b) only ice will be formed. Once at the eutectic conditions, ice and $Na_2SO_4{\cdot}10H_2O$ will be formed (arrows c) in a particular ratio following the lever rule: mass of ice formed once at the eutectic point × distance "e" = mass of hydrated salt × distance "f". For optimal performance of the first crystallizer, it is advisable that there be at a maximum 30% of solids within the crystallizer; therefore, a mother liquor at the eutectic concentration will be present. Inside the reactor a gravitational separation of ice and decahydrated salt will take place. It is very important that students understand that ice is also formed along path "b" which is different to that formed once at the eutectic point. Ice is one of the desired products of the plant and can be taken out. On the other hand, the hydrated salt will need additional transformation.

A second crystallizer will convert $Na_2SO_4{\cdot}10H_2O$ to Na_2SO_4 by means of heating. The path followed in the second crystallizer is shown in Fig. 5. Initially, pure hydrated salt will be warmed above the equilibrium solid line Na_2SO_4–$Na_2SO_4{\cdot}10H_2O$ (path g). Once there, a saturated solution will form that is in equilibrium with the anhydrous salt (path h). The proportion in which these two new phases form

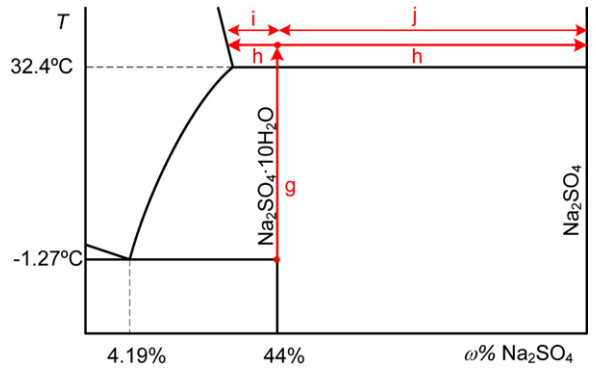

Fig. 5 – Path followed in the Na_2SO_4–water equilibrium phase diagram by the hydrated salt stream in the second crystallizer (after Hougen et al., 1954).

(saturated solution and anhydrous salt) is again dictated by the lever rule: mass of saturated solution × distance "i" = mass of anhydrous salt × distance "j". We have already obtained the other product of the plant, anhydrous salt. If, for instance, the temperature of the second crystallizer is set to 33 °C, then the saturated solution will have a concentration of 33% (information obtained by consulting a complete phase diagram). Since the 33% saturated solution cannot leave the plant as an exit stream, it then needs to be recycled.

Because it would be better to make use of the ice to cool down the warm stream entering the first crystallizer, the proposed flowsheet diagram is the one shown in Fig. 6. The streams have been allocated the numbers shown in Fig. 7 for easy referencing.

In view of the extensive discussion above, we can assert that we have gathered a substantial amount of information. This is collected in Table 1. The rest of the table needs to be filled in based on mass balances and equilibrium equations.

3.2. *Mass balances and equilibrium equations*

In order to complete Table 1, the following approach was taken. The 4 Tm/day of dissolved Na_2SO_4 entering through stream 1 must leave in stream 9 as a solid. Stream 5 contains only $Na_2SO_4{\cdot}10H_2O$, this means that streams 8 must contain the equivalent amount of saturated solution at 33%. By using the lever rule:

$$M_8 \times (0.44 - 0.33) = M_9 \times (1 - 0.44) \quad (1)$$

where M_8 and M_9 are total mass flow rate of streams 8 and 9. By solving Eq. (1) the value for M_8 can be obtained.

A total mass balance around the second crystallizer ($M_5 = M_9 + M_8$) gives us the total mass flow rate of stream 5. Now, streams 8 and 1 mix producing stream 2. A mass balance around the mixer ($M_2 = M_8 + M_1$) gives the value of the mass flow rate of stream 2. Knowing M_2, it will be easy to obtain its mass fraction from a salt mass balance around the mixer ($M_1\omega_1 + M_8\omega_8 = M_2\omega_2$). Solving for ω_2 we find that the mass fraction of Na_2SO_4 is 0.09, to the right of the eutectic point. The reasoning now changes with respect to what was initially discussed, but it will be very similar: before the eutectic point can be reached, some $Na_2SO_4{\cdot}10H_2O$ must first solidify.

Inspection of Fig. 7 shows that stream 3 is the same as stream 2 but only cooler. Thus, from stream 3s concentration to the eutectic concentration, some hydrated salt will be formed and only then will some ice in equilibrium with the new hydrated salt solidify. Since this is a tricky part it might help to break the real process taking place in the first crystallizer into two *fictitious* stages like that shown in Fig. 8. Let's denote by M_3' a fictitious liquid stream 3 (see Fig. 6) which has reached the eutectic point *before* any ice has formed. This fictitious situation does not exist but it helps to visualize it that way to account more easily for all the solidification that takes place in the first crystallizer. Also, let's denote by S (see Fig. 8) another fictitious solid stream of hydrated salt.

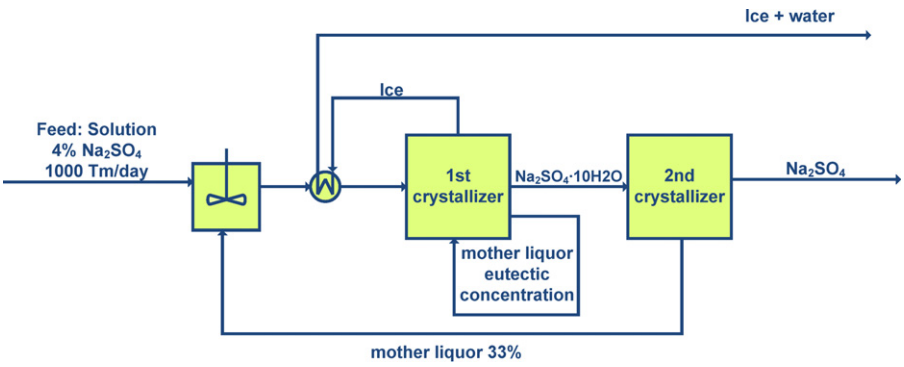

Fig. 6 – Proposed flowsheet diagram for the plant under design.

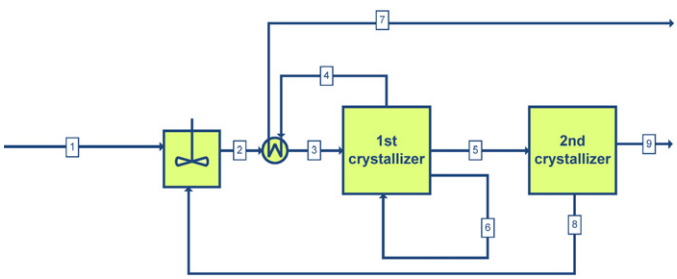

Fig. 7 – Proposed flowsheet diagram indicating stream numbers for easy reference.

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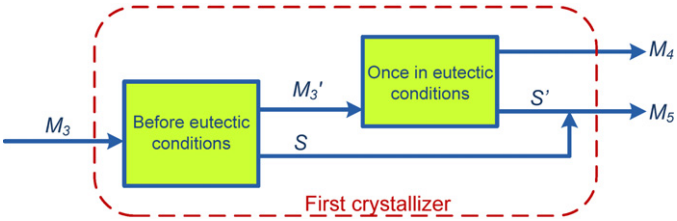

Fig. 8 – Fictitious representation of the first crystallizer to facilitate solving the mass balance. S refers to the salt formed between stream 3s conditions and the eutectic point. The liquid M_3' refers to the difference between M_3 and S.

Table 1 – Preliminary information deduced from the phase diagram and overall mass balance.

	Stream								
	1	2	3	4	5	6	7	8	9
Flowrate (Tm/day)	100			96			96		4
ω% Na_2SO_4	4			0	44	4.19	0	33	100

Table 2 – Completed mass balance table.

	Stream								
	1	2	3	4	5	6	7	8	9
Flowrate (Tm/day)	100	120.2	120.2	96	24.2	280	96	20.2	4
ω% Na_2SO_4	4	9	9	0	44	4.19	0	33	100

From Fig. 8 we already know the value of $\omega_{3'}$ (the eutectic concentration) and that of ω_S in addition to the concentration of Na_2SO_4 inside $Na_2SO_4{\cdot}10H_2O$ as explained in Section 2.2.

$$\omega_S = \omega_5 = \frac{\text{MW of } Na_2SO_4}{\text{MW of } Na_2SO_4 \cdot 10H_2O} = 0.44 \quad (2)$$

Now, a salt balance around the first unit in Fig. 8 ($M_3\omega_3 = M_3'\omega_{3'} + S\omega_S$) together with a total mass balance around the same unit ($M_3 = M_3' + S$), will provide us with the values of M_3' and S.

Thus, once at the eutectic point (second unit in Fig. 8), the ratio of ice to hydrated salt produced is a fixed value given by the solubility chart. The red lines "e" and "f" plotted in Fig. 4 show the distances for the lever rule calculation

$$M_4 \times (0.0419 - 0) = S' \times (0.44 - 0.0419) \quad (3)$$

From Table 1 it was already known that M_4 is 96 Tm/day (from the overall mass balance), therefore a value for S' can be obtained.

Finally, M_5 can be obtained from a mass balance around the second unit in Fig. 6 ($M_5 = S + S'$). It is always advisable for students to check all answers. In this case, M_5 could also be obtained from the total mass balance around the second crystallizer ($M_5 = M_9 + M_8$). These two results must obviously agree. Table 2 presents the full mass balance results.

4. Another set of problem statements

The solved problem presented here could be adapted or not and be used at different levels of the chemical engineering curriculum. For instance, it could be given directly to senior students registered for an elective course on crystallization.

This EFC problem statement could be adapted and simplified for first year students so that the emphasis is on the phase diagram and mass balances with only one crystallizer and no recycle stream. Table 3 shows some statements suited to the first year level.

Also, this problem could be set as a final year (or design) project. Table 4 shows an example of a project proposal.

Table 3 – Set of questions about EFC adapted for first year students.

Question 1.—A batch crystallizer contains a solution of 4 wt.% Na_2SO_4 at 15 °C.

1a. Use the phase diagram to identify the eutectic point conditions for this salt.

1b. At which equilibrium temperature will the mixture begin to solidify? Which solid is the first to be formed?

1c. Repeat question 1b for a feed at 30 °C containing 10 wt.% Na_2SO_4

1d. Which solid is the first to be formed under EFC conditions?

Question 2.—A crystallizer operating under continuous conditions is fed with 100 Tm/day of solution at 4 wt.% Na_2SO_4 at 15 °C. If the crystallization were to occur under eutectic conditions (EFC), and the crystallizer must not contain more than 30% of solids, which components have to leave the crystallizer for a steady state to be reached? What are the mass flow rates of the components leaving the crystallizer?

Table 4 – Final year project proposal on EFC.

Design a plant to separate Na_2SO_4 from water by means of EFC. Feed information follows: 100 Tm/day of solution at 4 wt.% Na_2SO_4 and 15 °C. For environmental and economic reasons, only two streams should leave the plant, 4 Tm/day of anhydrous Na_2SO_4 and 96 Tm/day of water. The proposed solution must contain all flow diagrams (block flow diagram, process flow diagram and piping and instrumentation diagram), energy requirements for the plant, calculation of the crystallizers' sizes, the design of ancillary equipment and plant utilities, budget, project planning, layout and economic and environmental evaluation.

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5. Conclusions: some pedagogic considerations

This paper presents a solved problem of how to deal quantitatively with crystallization problems below the eutectic temperature. This content could be used to expose students to the novel technique of EFC and its possible application in the treatment of brines. It is also proposed as an excellent pedagogic complement for chemical engineering undergraduates because it combines mass balances with navigating a solubility diagram.

Our experience with undergraduate students is that lecturing them on the particularities of EFC is just another aspect inside the field of crystallization and they generally grasp the concept well. A survey done this year at the University of Alicante (Spain) reveals that 78% of students feel confident that they completely understand phase diagrams and the mass balances based on them. The remaining 22% declare that they still find it a little bit challenging. The same survey also conducted at the University of Cape Town this year gave similar percentages (83% and 17%). Among other questions about crystallization, we also asked them for their personal opinion on EFC and the general answer students gave was that they believe that it appears to be an effective process in the area of water treatment, but that further studies are required in order to see if it will or not be a profitable process.

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