

The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and Mark A. Burns, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

PRACTICAL APPLICATIONS OF MASS BALANCES AND PHASE EQUILIBRIA IN BRINE CRYSTALLIZATION

M.E. TABOADA, T.A. GRABER
Universidad de Antofagasta
Casilla 170, Antofagasta, Chile

Mass-balance applications and a good level of phase-equilibrium knowledge, among other things, are required for a full understanding of brine-crystallization phenomena. Brine multi-component systems are complex, and phase diagrams are useful tools for explaining their behavior and designing crystallization processes. In the problem presented here, mass balances and phase-equilibrium criteria are combined to solve a practical application that is suitable for classroom presentation.

Maria E. Taboada is an assistant professor of chemical engineering at the University of Antofagasta. She received her BTech (1980) from the Universidad Católica del Norte and her MS (1989) from the Universidad de Chile. Her areas of interest are in process crystallization.



Teofilo A. Graber is an associate professor in chemical engineering at the University of Antofagasta. He received his BTech (1975) from the Universidad Técnica del Estado and his MS (1988) from the Universidad de Chile. His research interests are in chemical processes.



© Copyright ChE Division of ASEE 1994

PROBLEM

A chemical plant is being planned for the manufacture of anhydrous sodium sulphate in crystalline form, starting from a saturated aqueous solution at a temperature of 25°C. For process-design purposes, we have available a binary solubility diagram for Na₂SO₄—H₂O,^[1] and a ternary solubility diagram for Na₂SO₄—NaCl—H₂O at 25°C.^[2] From the available information, suggest different alternatives for the production process, indicating in each case the final mass of anhydrous sodium sulphate, based on 1,000 kg of feed solution.

SOLUTION

Three processes for obtaining the desired result will now be presented.

ALTERNATIVE 1 Cool, then dry crystals.

As shown in Figure 1, point **F** denotes the feed solution at 25°C. The overall process is shown diagrammatically in Figure 2. The cooling process, which ends at 5°C, is represented by the line **Fa**. Point **a** is in the two-phase zone, with points **b** and **c** representing the solution and crystal phase, respectively.

An initial solution of mass $F = 1,000$ kg is considered. Total substrate and total mass balances then give

$$F = S + C \quad (1)$$

$$FX_F = SX_S + CX_C \quad (2)$$

Here, C and S are the masses of the crystal and solution, respectively.

From Figure 1, the following mass fraction values, denoted by X with appropriate subscripts, are obtained:

- (a) $X_F = 0.22$
- (b) $X_S = 0.06$
- (c) $X_C = 0.44$

The amount of the decahydrated sodium sulphate mass can be calculated from a combination of Eqs. (1) and (2):

$$C = 421 \text{ kg Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$$

As *anhydrous* crystals are the desired final product, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ must be subjected to a drying process, resulting in 185 kg of Na_2SO_4 . Most impurities that are present in the initial solution will remain in the mother liquor.

ALTERNATIVE 2

Heat, then vacuum evaporate

The overall process is presented in Figure 3. The initial solution is first heated to 40° , and then, under vacuum evaporation, 90% of the water is eliminated. Referring to Figure 1, F is again the starting point, and **Fd** and **dg** represent the heating and evaporation steps, respectively. If V denotes the mass of the water evaporated, the total mass balance is

$$F = S + C + V \quad (3)$$

The solute balance is similar to Eq. (2), although the mass values are different. Considering that the mass of evaporated water is 90%, then $V = 702 \text{ kg}$. A combination of Eqs. (2) and (3) then gives

$$FX_F = (F - C - E)X_S + CX_C \quad (4)$$

Since anhydrous salt is the end product of this process, $X_C = 1$. The corresponding saturated solution is designated by point **e**, so that $X_S = 0.33$. The mass of Na_2SO_4 crystal is $C = 181.6 \text{ kg}$. Again, most impurities remain in the mother liquor.

ALTERNATIVE 3

Add NaCl to crystallize

As a third option, summarized in Figure 5, the same initial saturated solution **F** is mixed with sodium chloride at 25°C , this salt and aqueous system now being represented by the *ternary* diagram of Figure 4. Referring to Figure 4, the selected process is a result of mixing the initial solution **F** with sodium chloride, producing a two-phase mixture represented by the point **p**. The two components of this mixture are a saturated solution

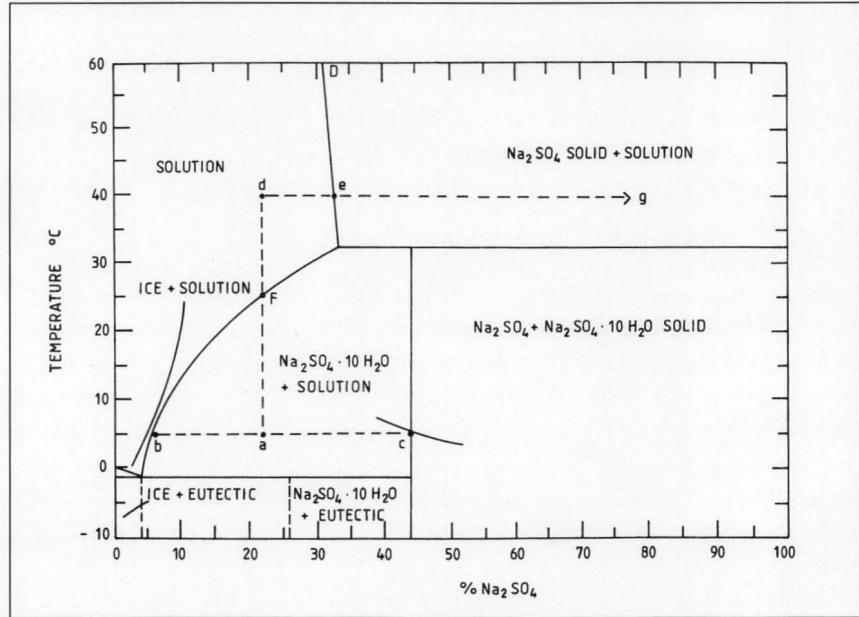


Figure 1. Phase Equilibrium $\text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$

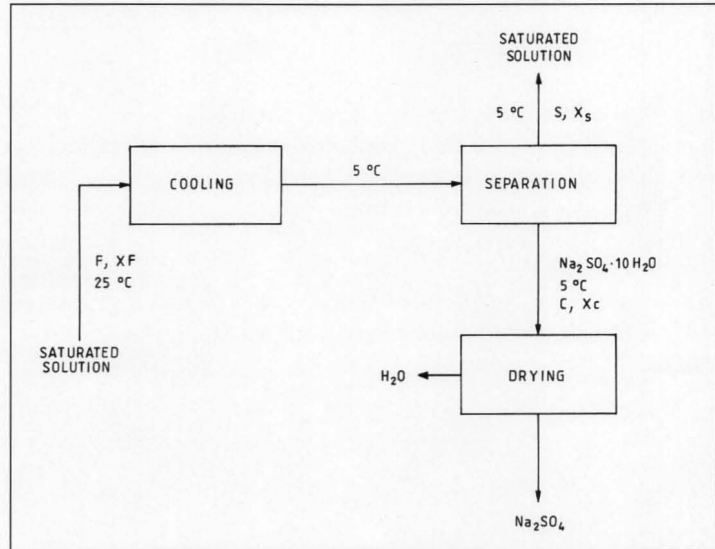


Figure 2. Flowsheet Alternative 1

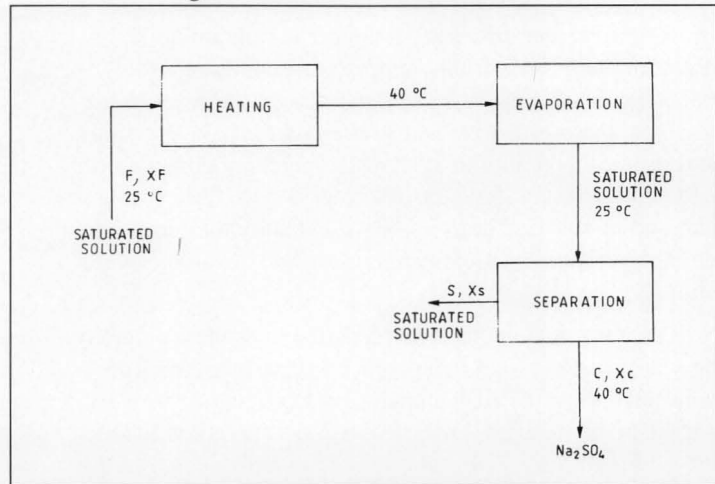


Figure 3. Flowsheet Alternative 2

s and crystallized sodium sulphate. Point **p** should be as close as possible to the tieline **b-Na₂SO₄**, in order to obtain a maximum amount of crystals, which is proportional to the ratio

$$\frac{\overline{sp}}{\overline{pNa_2SO_4}}$$

The final point **p** in Figure 4 must fall within the two-phase area **a-b-Na₂SO₄**, denoted as "γ"; in this way the amount of salt to cause crystallization can be determined. This process, in which a third component is added to displace the saline equilibrium, is termed *salting-out*.

The mass-balance calculations are made from Figure 4 by the *center-of-gravity* or *ratio-scale-moment* method.^[3] The mass N of sodium chloride that is required can be calculated by considering the proportionality between the masses of the streams, giving

$$N = F \left(\frac{\overline{Fp}}{\overline{pNaCl}} \right) \quad (5)$$

In Figure 4, the line-segment ratio $\overline{Fp} / \overline{pNaCl}$ is 0.234. Thus, the required mass of sodium chloride is 234 kg, and, considering a total mass balance, the mass P of the solution at point **p** is obtained:

$$P = F + N = 1,234 \text{ kg} \quad (6)$$

By a similar procedure, the mass C of Na₂SO₄ crystal can be obtained as follows:

$$C = P \left(\frac{\overline{ps}}{\overline{sNa_2SO_4}} \right) = 128 \text{ kg} \quad (7)$$

CONCLUDING REMARKS

The creativity of the student is stimulated as a result of examining the different strategies for obtaining sodium sulphate by various alternative combinations of unit operations. For each such alternative, there are associated mass balances and phase-equilibrium equations, and operating conditions such as temperature, composition, and total mass of product. In order to discover the best alternative, this problem can be extended by the further use of energy balances, equipment design, and economic evaluations.

In the chemical engineering department at the University of Antofagasta, it is normal practice to give homework problems involving the development of mass and energy balances, to be verified later in the Crystallization Laboratory.^[4] Finally, it is important to note that the design of this problem corresponds to a general policy regarding a link

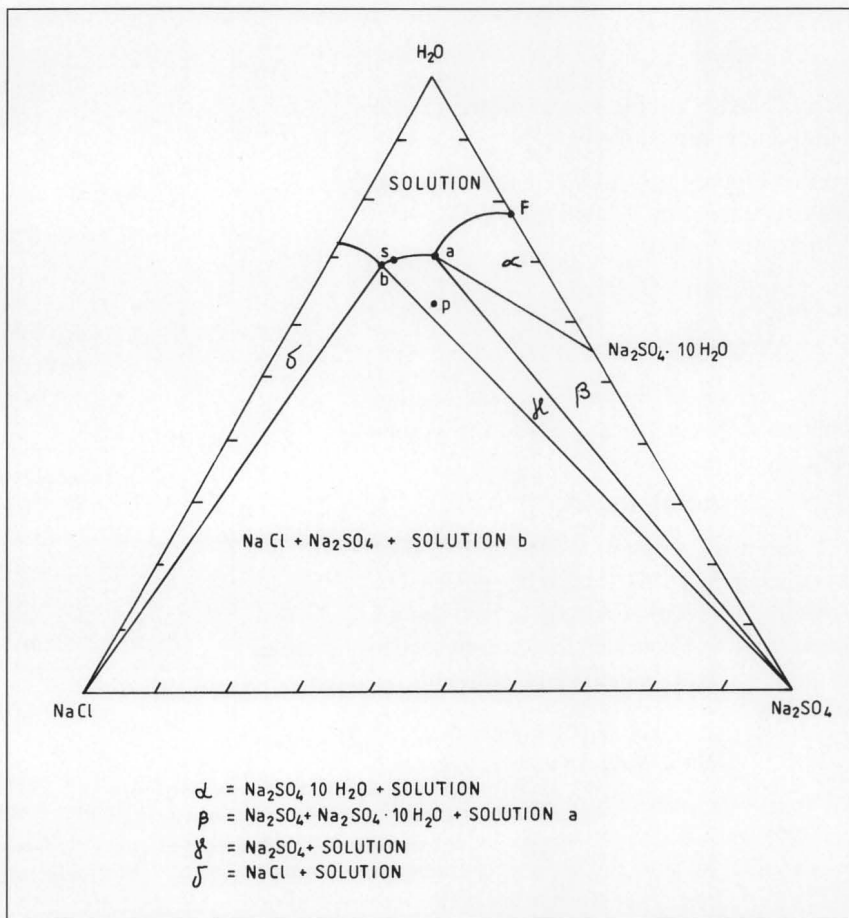


Figure 4. Phase Equilibrium NaCl - Na₂SO₄ - H₂O

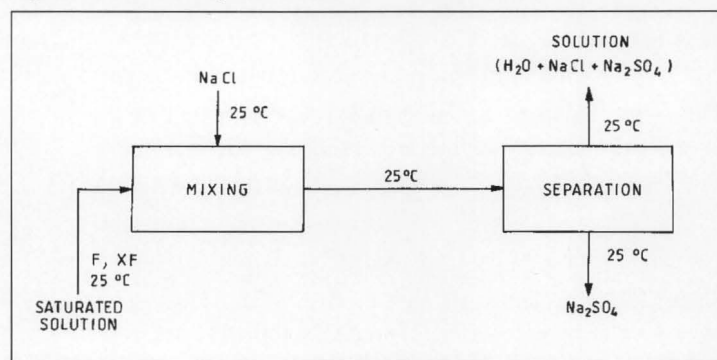


Figure 5. Flowsheet Alternative 3

between industrial reality in the North of Chile and the chemical engineering curriculum.

REFERENCES

- Hougen, O.A., K.M. Watson, and R.A. Ragatz, *Chemical Process Principles: Part I. Material and Energy Balances*, Wiley & Sons Inc., New York, NY (1975)
- Seidell, A., *Solubilities: Inorganic and Metal-Organic Compounds*, American Chemical Society, Washington, DC (1965)
- Bryant, F., "How to Design Fractional Crystallization Processes," *Ind. Eng. Chem.*, **62**(12) (1970)
- Graber, T.A., and M.E. Taboada, "Crystallization: An Interesting Experience in the ChE Laboratory," *Chem. Eng. Ed.*, **25**(2) (1991) □

INTERACTIVE COMPUTER GRAPHICS

Continued from page 115.

expands his or her understanding of the subject. "Simulation Graphics" does both. Not only are the tedious details of manual graphic design eliminated, but also the scope of assignable problems is greatly increased, even to include open-ended examples where students must search through many solutions to satisfy a constraint or find some optimum.

An advantage also arises from exposing students to computer-based visualization. Chemical engineering has moved less rapidly than other engineering fields to capitalize on the enormous conceptual boost offered by visual thinking—particularly in the classroom.^[15] Visualization models abound in thermodynamics, in transport phenomena, in reactor design, and in other core areas of the discipline.^[16-18] This application to graphical models of staged processes is a natural and significant step toward accelerating that movement.

A CLOSING NOTE

Over seventy years ago, Marcel Ponchon^[1] described his graphical method for binary distillation design. His introductory remarks, translated in part below, are as valid today as they were then. The efforts reported here and by those working before us have attempted to make those ideas more accessible through modern computer graphics.

The theory of distillation columns is rather complex, requiring long and difficult calculations. But it is possible, without going into the theory, to replace those calculations with graphical constructions that permit the solution of a rather large number of problems.

ACKNOWLEDGMENTS

Support for this work came from Iowa State University, Union Carbide, and the Camille and Henry Dreyfus Foundation. Janet Rohler Greisch edited this paper and managed its production through the Engineering Publication and Communication Services in the College of Engineering. Kurt Plagge and Kurt Whitmore prepared the figures.

REFERENCES

1. Ponchon, M., "Étude Graphique de la Distillation Fractionnée Industrielle," *La Technique Moderne*, **XIII**, 20, 53 (1921)
2. Savarit, R., *Arts et Metiers*, **65**, 142, 178, 241, 266, 307 (1922)
3. McCabe, W.L., and E.W. Thiele, *Ind. Eng. Chem.*, **17**, 605 (1925)
4. Gaskill, W.C., "Analog/Hybrid Simulations in Chemical Engineering Education," MS thesis, Dept. of Chem. Eng., Iowa State University, Ames, IA (1979)
5. Calo, J.M., and R.P. Andres, *Computers and Chem. Eng.*, **5**(4), 197 (1981)

6. Golnaraghi, M., P. Clancy, and K.E. Gubbins, *Chem. Eng. Ed.*, **19**(3), 132 (1985)
7. Kooijman, H., and R. Taylor, *CACHE News*, **35**, 1, The CACHE Corp., Austin, TX, Fall (1992)
8. Fogler, H.S., and S.M. Montgomery, *CACHE News*, **37**, 1, The CACHE Corp., Austin, TX, Fall (1993)
9. Seader, J.D., W.D. Seider, and A.C. Pauls, *Flowtran Simulation: An Introduction*, 3rd ed., CACHE Corp., Austin, TX (1987)
10. Treybal, R.E., *Mass-Transfer Operations*, 3rd ed., McGraw-Hill, New York, NY (1980)
11. Kremser, A., *Nat. Petrol. News*, p. 43, May 30 (1930)
12. Wankat, P.C., *Equilibrium Staged Operations*, Elsevier, New York, NY (1988)
13. Gmehling, J., U. Onken, and W. Arlt, "Vapor-Liquid Equilibrium Data Collection," Vol. 1, Part 2b, DECHEMA (1978)
14. Walker, J., and A. Karlsen, "Continued Development of 'Simulation Graphics,'" undergraduate research projects, Dept. of Chem. Eng., Iowa State University, Ames, IA; in progress
15. Reklaitis, G.V., R.S.H. Mah, and T.F. Edgar, "Computer Graphics in the ChE Curriculum," The CACHE Corporation, Austin, TX (1983)
16. Jolls, K.R., M.C. Schmitz, and D.C. Coy, *The Chemical Engineer*, No. 497, p. 42, May 30 (1991)
17. Charos, G.N., P. Clancy, K.E. Gubbins, and C.D. Naik, *Fluid Phase Equilibria*, **23**(1), 59 (1985)
18. Bird, R.B., personal communication □

BOOK REVIEW: Networking

Continued from page 119

presented conceptual frameworks that help the reader to grasp *why* NETWORKING is so vital in today's rapidly changing and diverse environment, *what* needs to be done to be an effective NETWORKER, and *how* to develop their own NETWORKING prowess.

Many of the NETWORKING principles can come fairly easily to gregarious, highly self-motivated and self-confident people. However, for the other (~) 95% of us, the idea of initiating contact with friends, neighbors, friends of friends—*perfect strangers!*—can be intimidating to the point of paralysis! This book can help anyone muster the courage and conviction to become an effective NETWORKER.

Some people will prefer to work through this book on their own. Others will realize greater benefit by working with a partner or in groups (*e.g.*, AIChE). The reader should have time to contemplate many of the ideas presented and to complete the recommended assignments in order to maximize full learning potential. Dialog, discussion, and sharing ideas with others should also prove beneficial.

In summary, NETWORKING is an important life skill for all of us. This book will prove very valuable to everyone who reads it. It should be required by those responsible for educating young people who are preparing to enter the professional world. □