



# Eutectic freeze crystallization simultaneous formation and separation of two solid phases

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## Abstract

Eutectic freeze crystallization (EFC) separates aqueous inorganic solutions into pure water and pure salt. By operating at the eutectic point, ice and salt can be formed simultaneously as two separate phases. Two aqueous systems were investigated in batch and continuous crystallization experiments: copper sulfate (eutectic temperature 271 K) and mono-ammonium phosphate (269 K). Below the eutectic temperature, ice can be formed without any salt formation by seeding with ice seeds and solely salt is formed by seeding with salt crystals. When however, the solution is seeded with both salt and ice crystals, two distinct solid phases are formed: when the stirrer is turned off, ice rises and salt settles. This shows that EFC separates aqueous solutions into ice and salt as two distinct phases. Based on these results, a 15 l cooled disk column crystallizer (CDCC) has been built, designed to crystallize and separate both the solids simultaneously in a single apparatus. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Eutectic freeze crystallization; Aqueous systems; CDCC

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## 1. Introduction

### 1.1. Eutectic freeze crystallization

Eutectic freeze crystallization is a technique to separate aqueous solutions into ice and solidified solutes simultaneously by operating at the eutectic point [1,2]. In principle, both organic and inorganic aqueous solutions can be separated, but this work is aimed at the separation of the latter. A typical phase diagram of a water–salt binary system is

depicted in Fig. 1. Point D is the eutectic point. Cooling of a solution with a temperature and composition of point A, causes the temperature to decrease until point B is reached. At point B, ice is formed which increases the concentration of the liquid phase. The system follows the line B–C, which enlarges the amount of ice and further concentrates the liquid phase. At point D, the ‘ice line’ intersects the solubility line of the salt and its saturation concentration is reached. Further cooling will result in the simultaneous formation of ice and salt. These two solid phases are completely separated: no solid solutions and no inclusions are formed when the growth process is carefully controlled [3]. Furthermore, the density difference of

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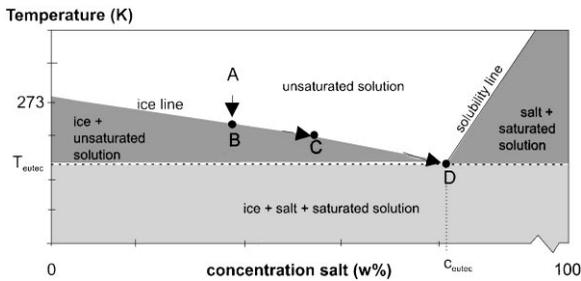


Fig. 1. Typical phase diagram for an inorganic aqueous binary system; point D ( $c_{\text{eutec}}$ ,  $T_{\text{eutec}}$ ) is the eutectic point.

ice and salt is typically in the order of  $1000 \text{ kg/m}^3$ , which makes the separation of these solids by force of gravity feasible. EFC is a separation technique that can be applied to most aqueous solutions of well soluble salts. Compared to evaporative crystallization, which is the conventional technique to separate well soluble salts, that have a solubility with a low-temperature dependence, from their solution, EFC requires less energy [4]. Cooling crystallization, which is also a comparable conventional technique, is limited by the remaining solubility at low temperature, whereas EFC would in principle be able to achieve a 100% separation of the solution into ice and salt, if no purge streams are needed.

## 1.2. Aim

The aim of this work is to experimentally validate the simultaneous formation of ice and salt crystals as two distinct separate solid phases in an indirectly cooled continuous suspension crystallizer. The model systems are  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ –ice and  $\text{NH}_4\text{H}_2\text{PO}_4$ –ice. Finally a new type of crystallizer will be presented that integrates the crystallization and the separation step in one piece of equipment.

## 2. Experimental procedure

### 2.1. Experimental setup

Experiments were performed in a 250 ml jacketed glass vessel (see Fig. 2). The crystallizer

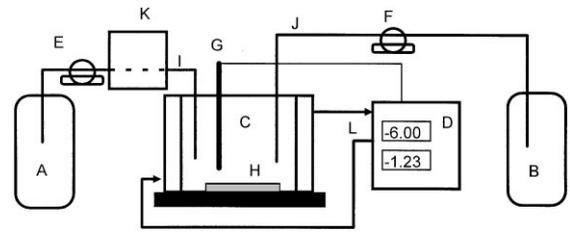


Fig. 2. Schematic representation of the experimental setup. A: feed storage; B: product storage; C: jacketed crystallizer; D: thermostatic cooler; E,F: peristaltic pumps; G: PT-100 temperature sensor; H: magnetic stirrer; I: feed liquid; J: product slurry; K: pre-cooling thermostat; L: cooling liquid.

was cooled indirectly with ethylene glycol. A LAUDA RK 8 KP thermostatic unit was used to cool the ethylene glycol and pump it through the jacket of the crystallizer. The temperature inside the crystallizer was measured with a PT-100 sensor connected to the RK 8 KP. Agitation in the crystallizer was provided by a magnetic stirrer. With continuous experiments, the feed was pumped into the crystallizer using peristaltic pumps. In the  $\text{NH}_4\text{H}_2\text{PO}_4$  experiments, a pre-cooling thermostat (LAUDA RC 20 CS) was used to pre-cool the feed before entering the crystallizer. The product slurry was pumped with a peristaltic pump to the storage vessel.

### 2.2. Batch experiments with $\text{CuSO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$

In the batch experiments, no feed and product streams were introduced in the crystallizer. The liquid in the crystallizer was supercooled 1.0 K below the eutectic temperature. With the temperature of the ethylene-glycol flowing through the jacket of the crystallizer kept constant, ice seeds were added. After waiting for about 1 h, the number of solid phases in the crystallizer was determined visually: when the stirrer is turned off, ice crystals float to the top of the crystallizer and salt crystals settle at the bottom. Then the crystallizer was heated until all solids vanished. Starting again with a clear liquid, the liquid was again supercooled and the experiment was repeated, but now with salt seeds.

### 2.3. Continuous experiments with $\text{CuSO}_4$

With a 16wt%  $\text{CuSO}_4$  feed stock, three experiments were done. To ensure the presence of both salt and ice crystals at the start of the continuous experiment, a start-up similar to the batch experiments was conducted. With the feed and product pump off, the temperature of the cooling liquid was set at 270.0 K. After waiting for about  $1\frac{1}{2}$  hr, the crystallizer temperature was constant: 271.0 K. There were no crystals present, the liquid was supercooled. At this point, ice and salt seed crystals were introduced in the crystallizer and the feed pump was started. The feed stream entered the crystallizer at room temperature, pre-cooler 'K' in Fig. 2 was not used with the  $\text{CuSO}_4$  experiments. The product pump worked semi-continuously. In this way, classification of the crystal slurry at the outlet was avoided by using a high flow rate for a short time followed by a period where the pump is switched off. At various points in time, the number of phases present was checked by turning off the stirrer: ice floated to the top and salt settled at the bottom. The temperature of the suspension content was recorded with time.

### 2.4. Continuous experiments with $\text{NH}_4\text{H}_2\text{PO}_4$

These experiments were analogous to the continuous  $\text{CuSO}_4$  experiments, but now pre-cooler 'K' in Fig. 2 was used to supercool the 17wt%  $\text{NH}_4\text{H}_2\text{PO}_4$  feed stream to about 267 K before entering the crystallizer. The temperature of the cooling liquid of the crystallizer was 266.7 K.

## 3. Results

### 3.1. $\text{CuSO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ batch experiments

Starting with a clear, supercooled liquid and adding ice seeds results in the formation of ice crystals without formation of salt crystals. This is observed in both the  $\text{CuSO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  experiments. Also, in both systems, starting with a clear supercooled liquid and adding salt seeds results in formation of salt crystals without formation of ice crystals. The presence of either of the two

phases (or both at the same time) is easily determined by turning off the stirrer: salt settles and ice rises. Seeding with both ice and salt results in the formation of both ice and salt phases. This is accompanied by a gradual rise of the suspension temperature to the eutectic temperature in about 2 h. This temperature of the eutectic  $\text{CuSO}_4$ -water system was found to be 271.6 K, corresponding well with literature [5]. The temperature of the eutectic  $\text{NH}_4\text{H}_2\text{PO}_4$ -water system was 269.0 K.

### 3.2. Continuous experiments with $\text{CuSO}_4$

The temperature within the crystallizer versus time is depicted in Fig. 3. A photograph of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  product crystals at the end of experiment E3 is presented in Fig. 4. From this photograph, a growth rate of  $4 \times 10^{-8}$  m/s of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystals is estimated. Roughening of the crystal surface and rounding of the crystal edges is also observable from the photograph. This is the result of a large growth rate of the crystals. For comparison, MSMPR cooling crystallization experiments of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  performed by Zumstein and Rousseau [6], show crystals with smooth surfaces and sharp edges at a growth rate of  $1.4 \times 10^{-8}$  m/s. Strangely, the crystals reported by Zumstein and Rousseau are (slightly) agglomerated, whereas the crystals in Fig. 4 are not.

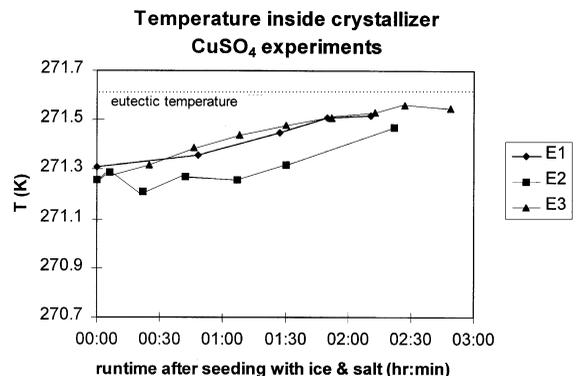


Fig. 3. Temperature inside the crystallizer for three  $\text{CuSO}_4$  continuous crystallization experiments. Residence time was 30 min.

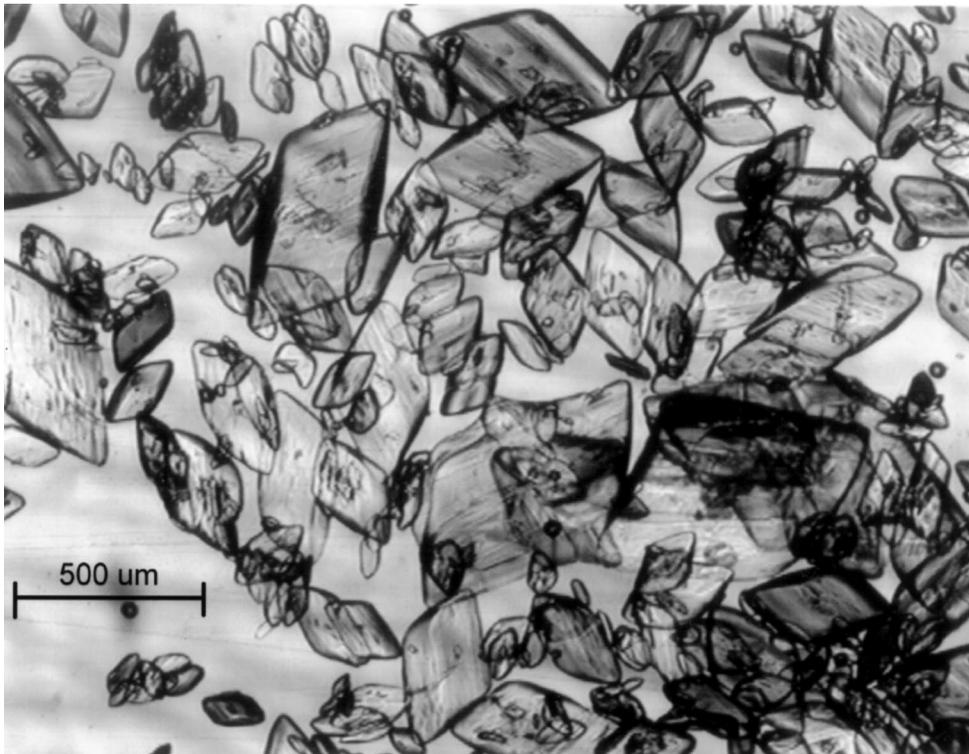


Fig. 4.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystals of experiment E3 taken at the end of the experiment.

### 3.3. Continuous experiments with $\text{NH}_4\text{H}_2\text{PO}_4$

Similar results are obtained for the  $\text{NH}_4\text{H}_2\text{PO}_4$  continuous experiments: two separate phases are formed. The temperature inside the crystallizer is depicted versus time in Fig. 5. The heat flux from the cooling liquid, through the wall of the crystallizer, to the suspension equals  $0.6 \text{ kW/m}^2$ , which is large enough to provide the necessary cooling in the crystallizer and small enough to prevent scaling of ice on the wall of the vessel.

### 3.4. Future research

Based on these results, a 15 l cooling disk column crystallizer (CDCC) has been built, capable of crystallizing and separating ice and salt crystals simultaneously in one apparatus. A schematic representation is given in Fig. 6. The CDCC is equipped with two cooling disks for indirect cooling of the column: cooling liquid flows through these

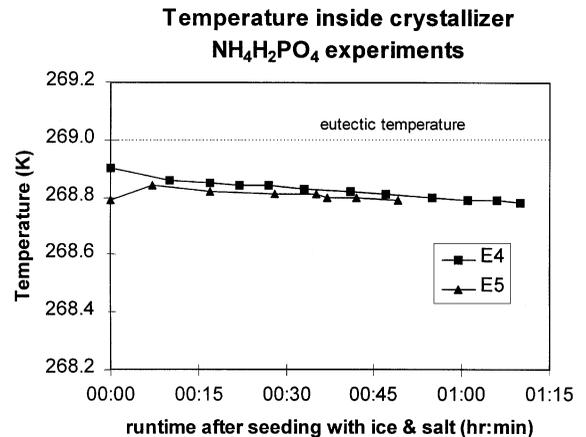


Fig. 5. Temperature inside the crystallizer for two  $\text{NH}_4\text{H}_2\text{PO}_4$  continuous crystallization experiments. Residence time was 20 min.

disks but is not in contact with the process fluid inside the column. The feed enters the column between the two disks. Ice and salt crystals are formed

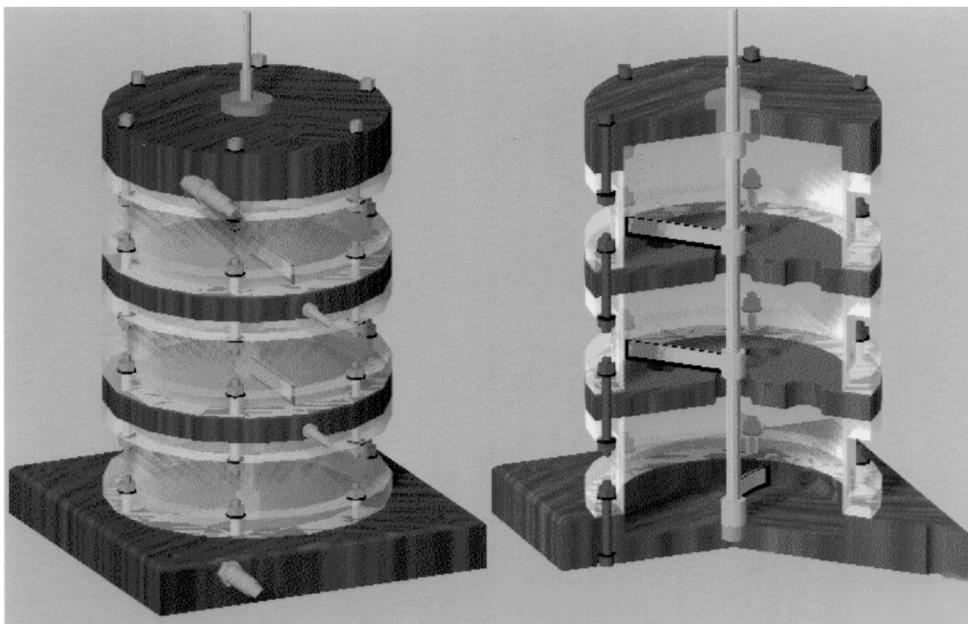


Fig. 6. Cooling Disk Column Crystallizer (CDCC).

and due to the density difference, ice rises and salt settles. The disks are provided with orifices, allowing the ice and salt crystals to either rise or settle through the disks. At the top of the column, ice is discharged. At the bottom of the column, salt is discharged. Preliminary experiments show promising results in the operation of the CDCC. In future, shape, size and purity of the ice and salt crystals will be investigated as a function of the cooling disk temperature, residence time and scraper speed.

#### 4. Conclusions

The eutectic temperature of  $\text{NH}_4\text{H}_2\text{PO}_4$ -water is 269.0 K. For  $\text{CuSO}_4$ -water the eutectic temperature is 271.6 K, corresponding with the value found in literature. Ice and salt ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{NH}_4\text{H}_2\text{PO}_4$ ) can be crystallized as two separate phases by continuous Eutectic freeze crystalliza-

tion. These two phases are readily separated by force of gravity.

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