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Purification of Acetic Acid Wastewater using Layer Melt Crystallization

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Abstract: Ice crystalline layers were prepared from a binary eutectic mixture of acetic acid and water using layer melt crystallization. The crystalline layers were obtained under the conditions of the cooling temperature at 269, 268, and 267 K, the feed compositions of 0.5, 1.0, and 5.0 wt% acetic acid, and the cooling rates of 0.1, 0.5, and 1.0 K/min. After crystallization, sweating operations were carried out for various crystalline layers obtained in crystallization. The effect of sweating on the impurity behavior inside crystalline layer was investigated. The crystalline layer formed in higher growth rate was purified more easily by sweating operations. Effective distribution coefficient in the sweating process was in the range of 0.2 to 0.01, which depended on the crystalline layers formed in crystallization process. Eventually, layer melt crystallization can be used for the treatment of acetic acid wastewater.

Keywords: Melt crystallization, acetic acid, wastewater, purification

INTRODUCTION

The technique for treatment of wastewater is an increasingly important subject in many processes of the chemical industry (1). A variety of wastewater treatment systems are used to produce the pure water from wastewater. Non-soluble separation techniques (e.g., sedimentation, flocculation, flotation, hydrocycloning, and filteration) and soluble separation processes

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(e.g., biological processes, adsorption, oxidation, membrane processes, evaporation, and melt crystallization) were used (2).

Recently, a wastewater containing acetic acid was discharged from the diverse manufacturing processes, such as terephthalic acid process (as solvent), cellulose acetate, dimethyl phthalate, isophthalic acid, and acetic anhydride (as by-product). Moreover, concentration of wastewater discharged from these processes containing the acetic acid was usually less than 5 wt%. Due to the low concentration and the corrosive properties of the wastewater, the evaporation of enormous volume and the intensive usage of the fossil fuel were the pivotal point to determine the economic feasibility of the wastewater treatment facilities. Despite the extensive literature on the treatment of toxic, corrosive waste, the technical demand for a cost effective and environmentally prudent method to treat pungent acidic waste is still increasing.

Layer melt crystallization of organic materials from the melt is used for the purification of chemicals at the cost of relatively low energy consumption compared to conventional separation techniques like evaporation (1–3). The use of melt crystallization for separation of chemical mixtures has increased rapidly in the chemical industry over the past few years. In melt crystallization, the purified compounds as well as the impurities are recovered in molten form and can be recycled, incinerated, or treated in some other way without an intermediate solvent removal step. From this point of view, melt crystallization is a clean technology for the separation of organics without using a solvent (4).

The crystals in layer melt crystallization are grown at cooled surfaces of the internal or external walls of the crystallizer. As the layer melt crystallizations are based on the growth of a solid layer on a cooled surface, the growth rate affects the structure of the layer and the inclusion of impurity in the layer (5, 6). In industrial applications, large growth rates are required for economic reasons. Therefore, entrapment of the impure liquid inclusions are inevitable. The amount of impurity can be reduced to some extent by controlling the growth conditions. The inclusions entrapped in the layer during crystallization are wholly inside the crystalline layer and cannot be removed by a purification method like washing. Therefore, an additional purification is essentially required for upgrading the crystal to ultra-purity after crystallization.

In the layer melt crystallization, the removal of entrapped inclusions upgrades of the purity of crystals. Sweating is desirable for upgrading the purity of crystalline layers after crystallization operations. Thus, the sweating process is effective for purification of crystals obtained in crystallization in industrial processes (7, 8). Although many previous works presented purification of crystals by sweating, most studies concentrated on the influences of sweating temperature (7–9). Moreover, many basic parameters that are necessary in the design of melt crystallization processes are difficult to predict, thus limiting the scale-up possibilities and the quality of the process design in many cases.

In this paper, layer melt crystallization and sweating operations were carried out for acetic acid-water mixtures, which is a simple eutectic system. Optimum conditions were set for separation and purification of water from acetic acid wastewater. The operating parameters investigated were feed composition, cooling rate, and sweating conditions.

EXPERIMENTAL

The layer crystallization and sweating experiments were carried out in laboratory scale, in an apparatus as illustrated in Fig. 1. The equipment is made of stainless steel and consists of a jacketed tank with volume of 4 liters, connected to a thermostatic bath. The dimension of the crystallization plate, which is the cooling surface for the layer growth, is 25 cm long and 8 cm in width. It is internally cooled by means of a thermostatic bath, which enables to carry out programed cooling and heating. The temperature of the melt was monitored by means of thermocouples placed inside the tank, inside the cooling plate and at the external circulation baths. Testing solution was pre-cooled to about 283 K using refrigerator, and then was filled into the tank before each run (see Fig. 1).

Sweating experiments are carried out just after the layer growth experiments. Sweating involves heating the crystalline layer for a desired time by circulating heating media inside jacket. The sweating apparatus consists of system controlling temperature and system weighing the melt drained out. The melt draining out was made to flow down into the sampling bottle during the sweating. The amount of the melt drained out was measured every 30 min and its composition was analyzed by acid-base titration. The sweating vessel was set at a desired temperature of sweating. The crystalline

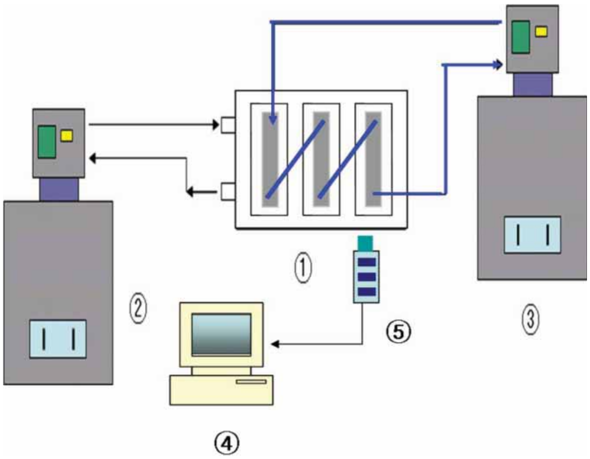


Figure 1. Experimental apparatus.

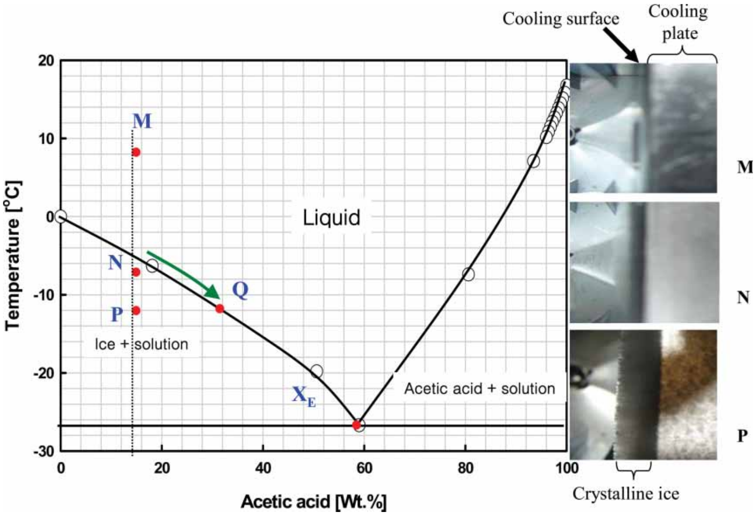


Figure 2. Solid-liquid phase diagram for acetic acid-water mixture and photographs of the crystalline layer during crystallization.

layer in the vessel gradually sweated and melt was drained into the sample bottle. The sweating temperature was 273 K.

Figure 2 shows examples of for the typical acetic acid-water phase diagram and photographs of cooling surface in the crystallizer during crystallization. If a solution started at point M approaches point N through a metastable zone, ice crystals start to be formed at point N. In the metastable zone, nuclei were formed and grew as needle-like crystals, which were then formed on the cold surface of crystallizer. At continuous cooling of the cooling surface, more ice crystals are grown and the residual solution will be more concentrated. The density of the crystalline layer could be controlled by the cooling temperature, feed composition, and cooling rate.

RESULTS AND DISCUSSION

Effect of Cooling Temperature

The growth rate for crystalline layer was controlled by adjusting the cooling temperature. Figure 3 shows a typical result for variation of layer thicknesses with elapsed time during crystallization. The crystallization was carried out by cooling the mixture with 1 wt% acetic acid at cooling temperatures of 269, 268, and 267 K. In Fig. 3, it was found that the crystalline layer thickness increases with elapsed time. The maximum growth rate, G_{max}, was calculated from the slope of plot of thickness against time at the beginning of

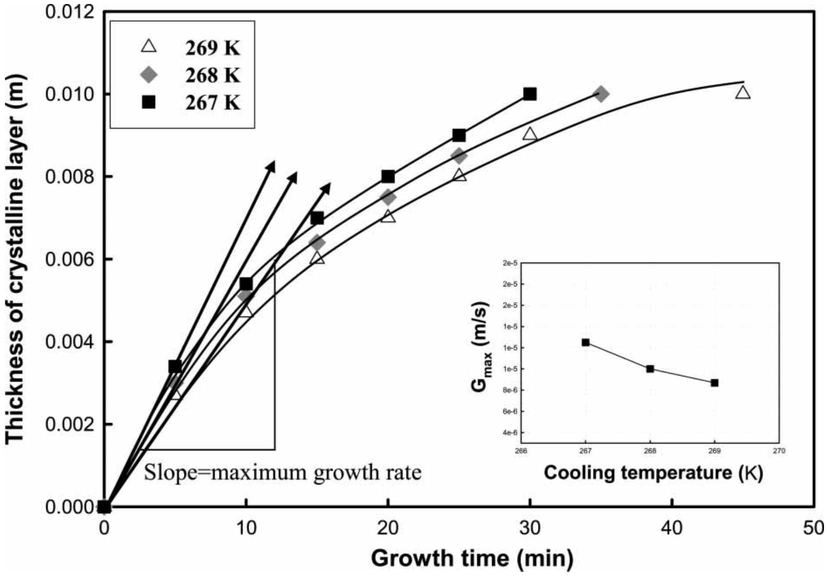


Figure 3. Variations of crystalline layer thickness with elapsed time at different cooling temperatures with 1 wt% acetic acid and plot of maximum growth rate versus cooling temperatures in layer crystallization operations.

crystallization. The maximum growth rate against the cooling temperatures was also shown in Fig. 3. It can be observed that the maximum growth rate increases with decreasing the cooling temperature. It suggests that lower cooling temperature leads to the higher supercooling (i.e. the driving force of crystal growth) (10).

Figure 4 shows the effect of sweating on the impurity content for the crystalline layers prepared at different cooling temperature. The crystalline layer was previously prepared at cooling temperatures of 269, 268, and 267 K for 1 wt% acetic acid mixture. The sweating process was then operated at a constant sweating temperature 273 K after draining of the residual melt obtained in crystallization process. In Fig. 4, before sweating, the impurity content of the crystalline layer is higher in the crystalline layer obtained at lower cooling temperature. This means that the lower cooling temperature results in the higher growth rate, which is due to the higher degree of supercooling. Eventually, the higher growth rates result in the larger amount of impurity inclusion. It supports that the high growth rates cause the crystal to grow rapidly, thus leading to imperfect crystals and a highly porous layer (1, 11). During the sweating of the crystalline layer, the amount of impurity included in the crystalline layer was gradually decreased with increase in sweating fraction. Impurity content was rapidly decreased at the beginning of sweating. This means that the impurity formed on growing crystals is mostly located on the surface of crystalline layer. When the sweating

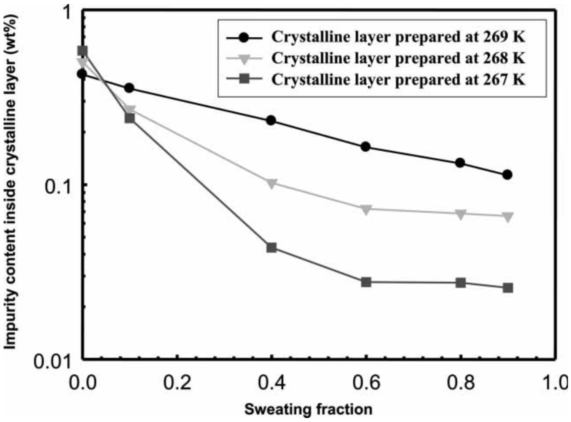


Figure 4. Variations of impurity content of crystalline layer in sweating process for the crystalline layers formed in various cooling temperatures.

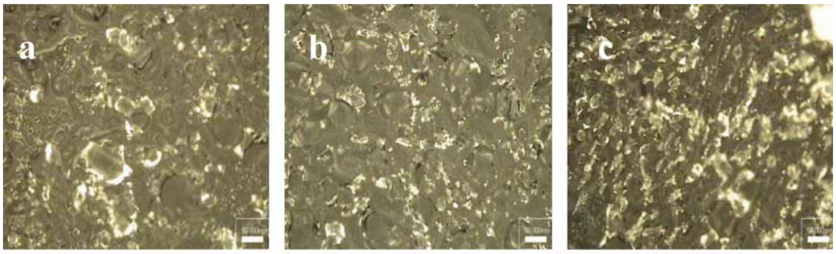
fraction was higher than 0.6, changes of the impurity inclusions were not considerable although the sweating operation still worked. In particular, despite different inclusion levels in the crystalline layer in the sweating process, the impurity content decreases faster in the crystalline layer formed in a higher cooling temperature. It means that the effect of sweating is higher in the crystalline layers with higher inclusions. Thus, it is concluded that for the higher separation efficiencies, crystallization at lower cooling temperature and sweating at higher temperature are considerable.

In addition, microscopic photos were taken to observe the sweating behavior for crystalline layers obtained at different cooling temperatures. The sweating effects can be also visualized by the microscopic photograph (Fig. 5). For the crystalline layer formed at the lower cooling temperature, the more melting spots were found in the sweating process.

Effect of Impurity Content

Figure 6 shows a variation of layer thickness against elapsed time during crystallization. Crystalline layers were formed by cooling mixtures with feed compositions of 0.5, 1.0, and 5.0 wt% acetic acid at the cooling rate of 1 K/min. The crystalline layer thickness increases with elapsed time. The maximum growth rate was plotted against the impurity contents of the feed. It was observed that the maximum growth rate decreased with increasing the impurity content of feed.

Figure 7 shows the plot of impurity content versus sweating fraction for the crystalline layers, which were formed in feed compositions of 0.5, 1.0, and 5.0 wt% acetic acid mixture at the cooling rate of 1 K/min. The sweating



269 K 268 K 267 K

Figure 5. Microscopic observation in course of sweating of the crystalline layers formed at various cooling temperatures.

process was then operated at a sweating temperature of 273 K after draining of the residual melt obtained in crystallization process. In Fig. 7, impurity content of crystalline layer obtained in the crystallization process (i.e., sweating fraction = 0) increases with increasing impurity content of the feed. In the sweating process, the impurity content of crystalline layer gradually decreases with increasing the sweating fraction. Despite different crystalline layers, the effect of sweating was almost similar because the slope of the plots were equalized. As a result, the effect of the feed condition of the crystallization process on the sweating could be neglected

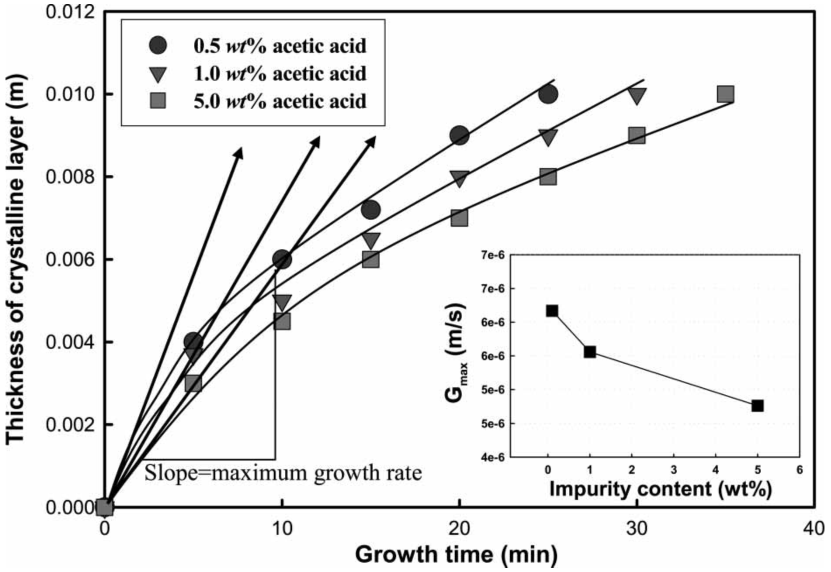


Figure 6. Variations of crystalline layer thickness with elapsed time in crystallization with different initial impurity contents at the cooling rate 1 K/min and maximum growth rate versus cooling temperatures in layer crystallization operations.

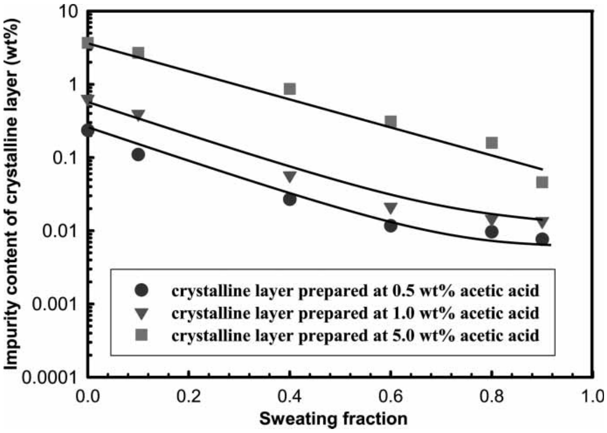


Figure 7. Variations of impurity content of crystalline layer in sweating process for the crystalline layers formed in different initial impurity contents.

even though the feed condition affected the impurity content of crystalline layer obtained in the crystallization process. From Figs. 6 and 7, growth rate decreases with increasing the impurity fraction of feed, while impurity inclusions before sweating increases with increasing the impurity fraction of feed. These two opposite factors would be combined in the sweating process.

Effect of Cooling Rate

Figure 8 shows variation of layer thickness with elapsed time during crystallization. The crystallization was carried out by cooling mixtures with 1 wt% acetic acid at cooling rates of 0.1, 0.5, and 1.0 K/min. In Fig. 8, it was found that the crystalline layer thickness increases with elapsed time. The maximum growth rate against the cooling rate is also shown in Fig. 8. It was found that the maximum growth rate was increased with increase in the cooling rate.

The effect of sweating fraction on the impurity content for different crystalline layers was shown in Fig. 9. The crystalline layers used were obtained at different cooling rates of 0.1, 0.5, and 1.0 K/min for 1 wt% acetic acid mixture. The sweating process was then operated at a sweating temperature of 273 K after draining of the residual melt obtained in the crystallization. In Fig. 9, before sweating, the impurity content of the crystalline layer grown at a higher cooling rate has slightly higher. Thus, the higher cooling rate induces the higher amount of impurity inclusion due to higher crystal growth rate. However, after sweating, the impurity content of the crystalline layer was gradually decreased with increase in sweating fraction. The impurity content decreases rapidly until sweating fraction is 0.4. This means that the impurity formed on growing crystals is mostly located on

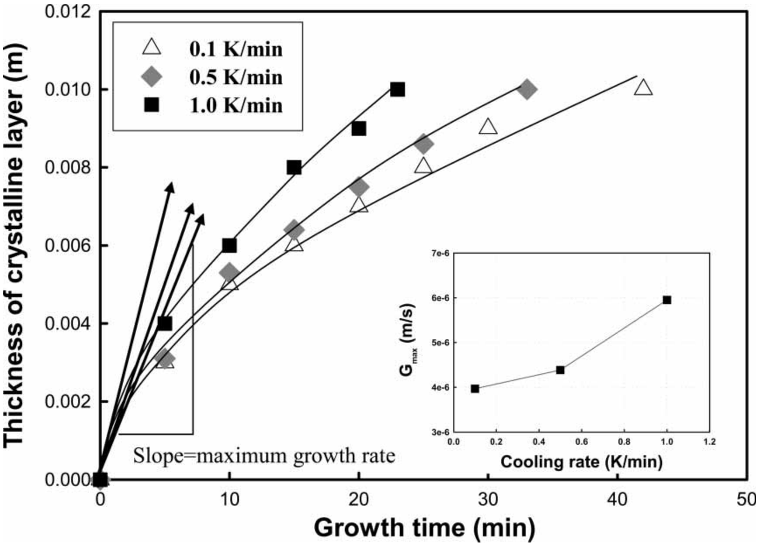


Figure 8. Variations of crystalline layer thickness with elapsed time in crystallization at different cooling rates and maximum growth rate versus cooling temperatures in layer crystallization operations.

the surface of crystalline layer. Then, at above sweating fraction of 0.8, changes of the impurity content were not considerable although the sweating operation was still at work. Impurity content decreases more rapidly in the crystalline layer formed in the higher cooling rate. This means that the higher growth rates cause the crystalline layer to grow more rapidly, thus leading to more imperfect crystals with a highly porous layer

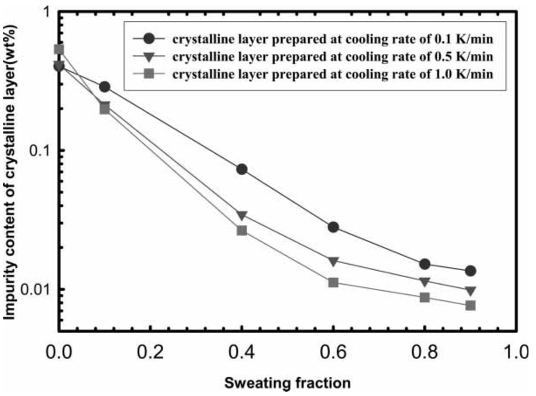


Figure 9. Variations of impurity content of crystalline layer in sweating process for the crystalline layers formed in various cooling rates.

(1). After sweating, the lowest impurity content in this layer was found to be 0.0076 wt% acetic acid for crystalline layer formed at cooling rate of 1.0 K/min. The result indicates that for the impurity inclusions inside crystalline layer, the sweating process has a positive dependence on the purification, while the crystallization process has negative dependence on that. Therefore, considering mechanisms of crystallization and sweating is necessary for an optimization of layer melt crystallization.

Impurity behavior depends mainly on the supersaturation because it affects the nucleation rate as well as the growth rate. In static melt crystallization, the cooling rate is an important parameter to affect the supersaturation. The supersaturation is related directly to the metastable zone width. The metastable zone width $\Delta T_{\max}$ was taken as the difference between the equilibrium temperature and the temperature at which nuclei were detected. Metastable zone widths for saturation temperature and cooling rate were plotted in log-log coordinates in Fig. 10. The plots are found to give a good straight line. These results show that the metastable zone width of the acetic acid increases with the cooling rate for all the experimental conditions explored. The relationship between metastable zone width $\Delta T_{\max}$ and cooling rate b is as follows:

$$\log b = \log k_n + n \log \Delta T_{\max} - \frac{1-n}{n} \log S \tag{1}$$

where k_n is a constant related to the nucleation rate and n is the nucleation order.

The values of the order of nucleation rate n and the constant of nucleatioin rate k_n in Eq. (1) were evaluated by regression analysis from the slopes and intercepts found in Fig. 10. The order of the nucleation rate is 2.08.

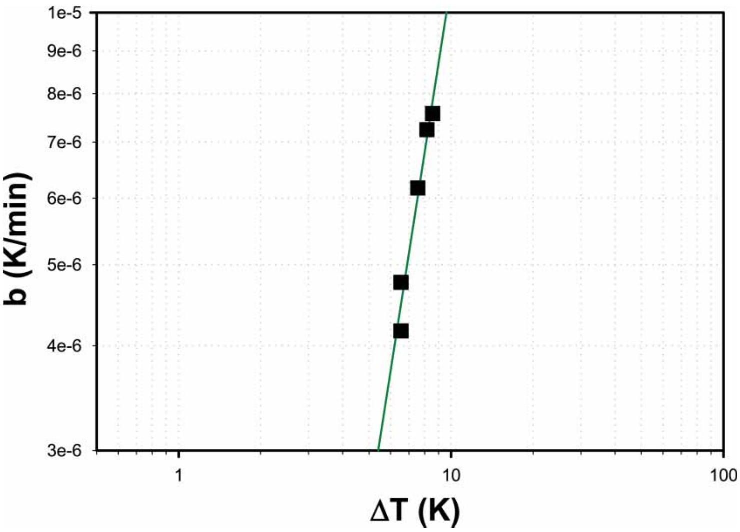


Figure 10. Plot of cooling rate against metastable zone width.

Separation Efficiency

The removal of acetic acid from acetic acid-water mixture is characterized by the effective distribution coefficient. The effective distribution coefficient *k* is defined by the ratio of mass fractions of impurity in the residual $\mathrm{x_{il}}$ and in the crystal x_{ic}.

$$k = \frac{x_{ic}}{x_{il}} \tag{2}$$

The effective distribution coefficient *k* close to 1 means that in a binary system almost no separation occurs, while *k* close to 0 means an almost perfect separation. Here $0 < k < 1$ is an essential condition of purification. Generally, the effective distribution coefficient k increases with increasing cooling rate and subcooling because they induce a high growth rate and thus cause the entrapment of impurities inside crystal. Therefore, the effective distribution coefficient depends on the crystallization conditions.

Figure 11 shows the effective distribution coefficients of sweating as a function of sweating fraction in sweating of crystalline layers obtained in the layer melt crystallization. The effective distribution coefficients of sweating were obtained for the crystalline layers obtained in the crystallization conditions that cooling temperatures, feed compositions, and cooling rates are in the ranges of 279 ~ 276 K, 0.5 ~ 5.0 wt%, and 0.1 ~ 1.0 K/min, respectively, under the sweating conditions investigated. A smaller distribution

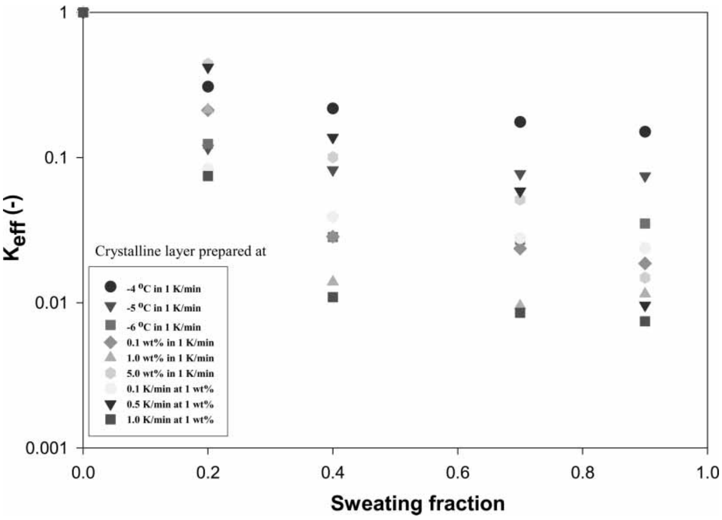


Figure 11. Distribution coefficients against sweating fraction in sweating for crystalline layers formed in various crystallization conditions.

coefficient of sweating was found in the crystalline layer obtained at lower cooling temperature, higher feed impurity content, and higher cooling rate, which leads to the higher growth rate. For crystalline layer before sweating, the effective distribution coefficients are equal to 1.0. As sweating proceeds, the effective distribution coefficients decrease continuously with increasing sweating fraction. As can be seen, the distribution coefficient at a sweating fraction of 0.4 was in the range of 0.2 to 0.01. In sweating the crystalline layer obtained at the cooling rate of 0.08 K/min, which was equivalent to the crystal growth rate of 10^{-8} m/s, its value was 0.01. Eventually, layer crystallization combined with the sweating process can be applied successfully to treat the acetic acid wastewater.

CONCLUSIONS

In this study, the purification of pure water from wastewater containing acetic acid was conducted by using layer melt crystallization. Ice crystalline layer was formed at various cooling temperatures, impurity contents, and cooling rates of an acetic acid mixture. The ice layer was purified by the sweating process. The acetic acid was successfully removed by layer melt crystallization combined with the sweating process. In this sweating process, an impure crystalline layer formed in higher growth rate is purified more easily. Effective distribution coefficient in the sweating process was in the range of 0.2 to 0.01, which depended on the crystalline layers formed in crystallization process. Eventually, layer melt crystallization can be used for the treatment of acetic acid wastewater.

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REFERENCES

1. Guardani, R., Neiro, S.M.S., Bülau, H., and Ulrich, J. (2001) Experimental comparison and simulation of static and dynamic solid layer melt crystallization. *Chem. Eng. Sci.*, 56: 2371.
2. Wakisaka, M., Shirai, Y., and Sakashita, S. (2001) Ice crystallization in a pilot-scale freeze wastewater treatment system. *Chem. Eng. Processing*, 40: 201.
3. Verdoes, D., Arkenbout, G.J., Bruinsma, O.S.L., Koutsoukos, P.G., and Ulrich, J. (1997) Improved procedures for separation crystals from the melt. *Applied Thermal Engineering*, 17: 879.
4. Kim, K.J. and Ulrich, J. (2002) A quantitative estimation of purity and yield of crystalline layers concerning sweating operations. *J. Crystal Growth*, 234: 551.

5. Ulrich, J., Bierwirth, J., and Henning, S. (1996) Solid layer melt crystallization. *Sep. Purif. Methods*, 25 (1): 1.
6. Delannoy, C., Ulrich, J., and Fauconet, M. (1993) *12th Symposium on Ind. Cryst.*, Warsaw, Poland.
7. Saxer, K. (1993) Proceedings of the 12th Symposium on Ind. Crys, Poland, 1013.
8. Matsuoka, M., Ohishi, M., and Kasama, S. (1986) Purification of *p*-dichlorobenzene and m-chloronitrobenzene crystalline particles by sweating. *J. Chem. Eng. Japan*, 19 (3): 181.
9. Ulrich, J. (1989) Purification by crystallization of organic compounds. In *Industrial Crystallization*; Nyvlt, J. and Zacek, S. (eds.); Elservier Science: New York, p. 585.
10. Chen, P., Chen, X.D.K., and Free, K.W. (1999) An experimental study on the spatial uniformity of solute inclusion in ice formed from falling film flows on a sub-cooled surface. *J. Food Eng.*, 39: 101.
11. Kim, K.J. and Ulrich, J. (2002) Impurity distribution in a solid-liquid interface during static layer crystallization. *J. Colloid and Interface Sci.*, 252: 161.