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Solid Layer Melt Crystallization

Joachim Ulrich[a]; Jutta Bierwirth[a]; Sabine Henning[a]
[a] Universität Bremen, Bremen, Germany

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SOLID LAYER MELT CRYSTALLIZATION

PRIV. DOZ. DR.-ING. JOACHIM ULRICH
DIPL.-ING. JUTTA BIERWIRTH
DIPL.-ING. SABINE HENNING
Universität Bremen
Verfahrenstechnik/FB4
Postfach 330440
D-28334 Bremen
Germany
Tel.: ++49/(0)421/218-2670
Fax: ++49/(0)421/218-5333

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1. Introduction

1.1 AIMS OF MELT CRYSTALLIZATION

Melt crystallization processes are predominantly used to separate and purify substances or to concentrate compounds. The thermal unit operation is based on a different equilibrium composition of a substance in a different stage of aggregation. Background information about the theory of melt crystallization can be found, e.g. in Mullin [1], Matz [2], Zief and Wilcox [3], Slown [4], Atwood [5], Ulrich [6,7], Jansens et al. [8] and Matsuoka [9].

In comparison with other separation technologies, e.g. distillation, the required energy for the phase change liquid/solid is much lower. This is due to the relatively low level of temperature and the much smaller latent heats. The energy required for the phase transition liquid/solid is only about 1/3 to 1/7 of the gas/liquid phase transition energy. Due to the low temperature level it is also possible to treat heat sensitive substances, like foods or polymers.

The separation technique melt layer crystallization does not need any additional substances like solvent as, e.g. in extraction. No further impurities get into the substance to be purified and no chemicals (solvent) have to be regenerated. So in comparison with extraction solvent recovery, capital and energy costs can be saved.

Another very important characteristic of melt crystallization processes is the high selectivity. Many mixtures to separate are eutectics with low solid solubility. For

these systems in theory only one crystallization step is necessary to recover a 100 % pure product. Since one component solidifies in pure form when the temperature of the melt is lower than the equilibrium temperature. Perfect crystals or crystal layers can only be obtained if the crystal growth rates are extremely slow and the necessary solid liquid separation after the growth process is perfect, too.

Matsuoka [10] showed that 54,3 % of all organic mixtures for which phase diagrams can be found are eutectic systems. Further 31,6 % belong to the group of molecular forming compounds and systems with peritectic and eutectic points. Only 14,1 % of all investigated substances belong to the group of solid-solution forming substances. For these systems only an enrichment of one component by melt crystallization is possible so that several steps would be necessary to achieve the desired purity. A multistage process offers the possibility of complete product recovery although the number of required stages increases rapidly as recovery approaches unity. For eutectic systems product recovery is limited while the achieved product purity can be very high.

In Figure 1 the typical phase diagrams of binary organic systems are shown.

Due to the increased demand for ultrapure materials and energy saving, the solvent-free melt crystallization technologies gained more importance in recent years. Most organic substances with melting points between -50 and +200 °C that do not decompose can be separated by melt crystallization. Suitable substances are, e.g. hexamethylene diamine, naphthalene, xylol and acrylic acid. The processes for caprolactam, adiponitrile and hexamethylene diamine are particularly important commercially (according to [11]).

Like in other separation processes the result of the separation or the attained product purity, respectively, depends on the properties of the substance on the one hand and the chosen process and process parameters on the other hand.

In melt crystallization solid layer and suspension techniques can be differentiated [12]. In solid layer crystallization, also called progressive freezing, crystals grow perpendicular to a cooled surface and form coherent layers while the heat of fusion is removed through the crystalline layer and the cooled wall. The layer crystallization is a kind of incrustation process, however, the incrustation is deliberately

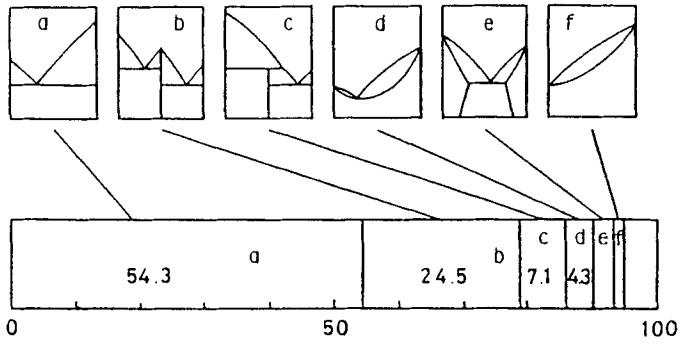

FIGURE 1: Phase diagrams of organic binary systems [10]

induced to obtain a purified product. Suspension processes are characterized by the fact that the crystals grow in the melt at a constant temperature just below the solidification temperature.

1.2 DIFFERENCES BETWEEN LAYER AND SUSPENSION GROWTH

The main differences between solid layer and suspension growth are summarized in Table 1. In comparison of the processes it is obvious, that the advantages of the one process are usually the disadvantages of the other and vice versa.

Melt crystallization processes are dominated by heat transfer. To have a driving force in solid layer process, the melt has to be subcooled through the wall of the cooled surface and later through the crystalline layer on top of it, too. After crystallization the residual melt is drained off and the crystal layer is melted.

Due to the high driving force and therefore high crystal growth rates, lot of contaminated liquid melt is entrapped in the solid layer so that the required purity is usually not attained in one step. As a consequence the process has to be repeated or further purification has to be performed, which decreases the overall efficiency.

In the case of suspension processes the crystals are surrounded by melt and the

TABLE 1: Comparison between solid layer and suspension crystallization from the melt

items	solid layer technique	suspension technique
melt temperature	above, but close to solidification temperature	below the solidification temperature
heat removal	through the crystal layer	through the melt
crystal growth rates	high 10^{-5} - 10^{-7} m/s	low 10^{-7} - 10^{-8} m/s
relative interface crystal-melt	small, about 10-10^2 m^2/m^3	large, about 10^4 m^2/m^3
apparatus	no moving parts except pumps and valves	moving parts
mass flow rate	large	small
incrustation problems	no	yes
transportation of product	easy, all liquid	problems, due to solids handling
solid-liquid separation	easy, just draining	difficult
scale-up	easy	difficult

system is almost isothermal at the crystallization temperature. Since the heat of fusion is only removed through the melt the subcooling can only be moderate. The crystals grow only at a low rate which leads, however, to a very pure product. In contrast to the suspension process the solid layer process shows nonadiabatic conditions and can lead up to 1000 times faster growth rates. High growth rates are necessary to compensate the lower production capacities due to the relatively small crystal growth area.

At the end of suspension crystallization processes the very pure crystals must be separated from the remaining, highly contaminated residual melt. This requires a solid-liquid-separation technique, e.g. filtration or centrifugation. Washing by pure melt and drying are often other necessary steps. Ultimately the quality of the concluding separation determines the effective purification result.

For many chemical applications the solid layer crystallization technique seems to dominate the market especially with regard to the high environmental safety, easy scale-up and the possibility to connect all process steps in one apparatus. The disadvantage of a lower purity in the crystallization step is taken into account, which is often more effective over all than a longer retention time or bigger volumes for the liquid phase in suspension techniques. A smaller volume leads towards less required space and smaller equipment which means less capital costs. Besides the purification efficiency of the crystallization process the yield of pure product is important for the competitiveness. In detail the volume-time-yield is the decisive criterion for the efficiency of the process. Often crystals with lower purity were produced by higher growth rates and post-crystallization steps are conducted to improve the product purity.

2. Basics of Solid Layer Melt Crystallization

Crystallization can be divided into two kinetic steps: the nucleation of crystals and the crystal growth.

The precondition for the growth of crystals is a nucleation step that can be heterogeneous or homogeneous. The most common way to start and maintain crystallization in solid layer techniques is to have a heterogeneous (roughnesses at the cooled surface) nucleation effect or a seeding procedure.

The driving force for crystal growth is the temperature gradient between the equilibrium melt temperature in front of the layer and the feed melt temperature ($\Delta T = T_{\infty} - T_{eq}$). During crystallization the heat of solidification is directly removed from

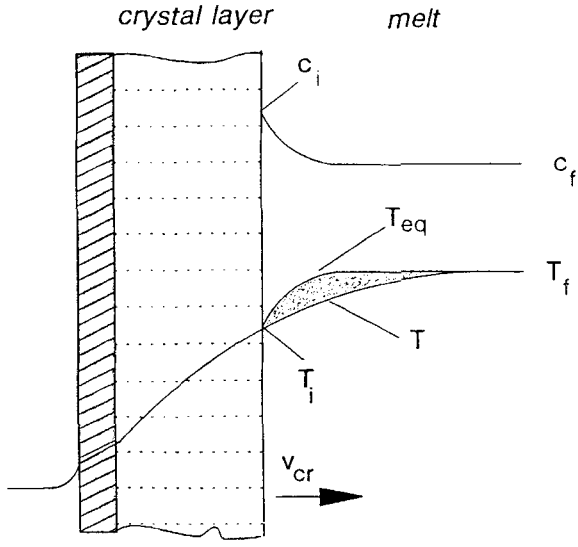

FIGURE 2: Constitutional Supercooling (shaded region)

the process through the crystal layer and the cooled surface. Therefore high growth rates can be achieved, which lead to an enrichment of impurities in front of the melt. According to the concentration gradient established, different local equilibrium concentrations exist in front of the layer, depending on the phase diagram and the temperature profile imposed within the boundary layer. Such effects cause additional driving forces and are called constitutional supercooling.

Constitutional supercooling occurs whenever the equilibrium melting point curve in the boundary layer in front of a growing crystal has a smaller gradient than the imposed temperature profile (Figure 2).

To avoid constitutional supercooling the imposed temperature gradient in the melt in front of the crystal interface has to be less or equal to the equilibrium temperature gradient according to the phase diagram. A further possibility to control the system is dissipative mixing in front of the growing crystal interface in the melt (e.g. by forced convection).

Whenever excessive constitutional supercooling is present, the growth of crystals will become dendritic. This causes the highly contaminated melt to be entrapped in the crystal layer in the form of liquid inclusions.

Liquid inclusions migrate due to the temperature gradient in direction towards the warm side, the melt. Wilcox [13], Polisaari et al. [14], Scholz [15] and Wangnick [16] found, that the migration of liquid inclusions and thereby the change in layer concentration, too, can influence not only the efficiency of crystallization but also the additional sweating and/or washing operations. Therefore the phenomenon of migrating liquid inclusions has to be considered whenever solid layer crystallization processes are investigated.

The product rate in layer crystallization depends strongly on the heat transfer properties of the solid phase. To obtain constant growth rates and thereby constant quality and product rates, the cooled surface has to be increasingly cooled since the crystal layer is growing and offering more thermal resistance.

The separation effect can be increased by post-crystallization treatments of the solid layer after the liquid melt is drained off. A measure for the separation efficiency is the effective distribution coefficient k_{eff}, defined as the ratio of the impurity concentration in the crystal layer c_{cr} and the impurity concentration in the feed (melt) c_{∞}:

$$k_{eff} = \frac{c_{cr}}{c_{\infty}} \quad . \tag{1}$$

A distribution coefficient equal to zero means perfect purification, whereas a distribution coefficient equal to one means no purification at all.

3. Process types of solid layer techniques

Possibilities to differentiate between the different techniques of melt crystallization are given by aspects like continuous versus batch or moving (flowing) versus stagnant melt that means static or dynamic processes, respectively (see Figure 3).

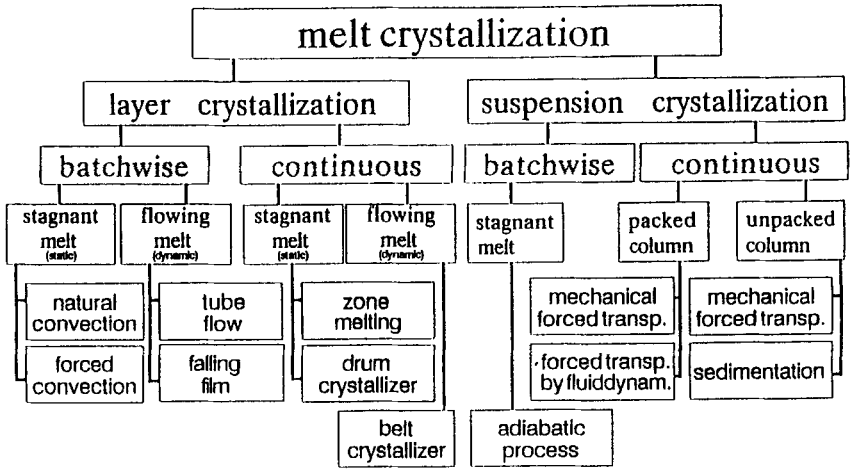

FIGURE 3: Melt crystallization - a differentiation [12]

Layer growth equipment published in patents or articles are shown in Figure 4.
In static equipment crystal growth occurs from a stagnant melt while in the dynamic case the melt is moved by external circulation. The same differentiation is possible for the suspension techniques. An overview of the available equipment is given in Figure 5.
Most suspension crystallizers for melt crystallization require crystals to be in the feed stream. In most cases these crystals originate from scraped crystallizers which are based on a solid layer created at the wall of the crystallizer's vessel and then scraped off by, e.g. a rotary steel blade.
More details of layer crystallization techniques will be given in the following.

3.1 STATIC PROCESSES AND APPARATUS

The solid layer techniques with stagnant melts are characterized by the fact that they possess a high safety in operation due to the simple equipment design.

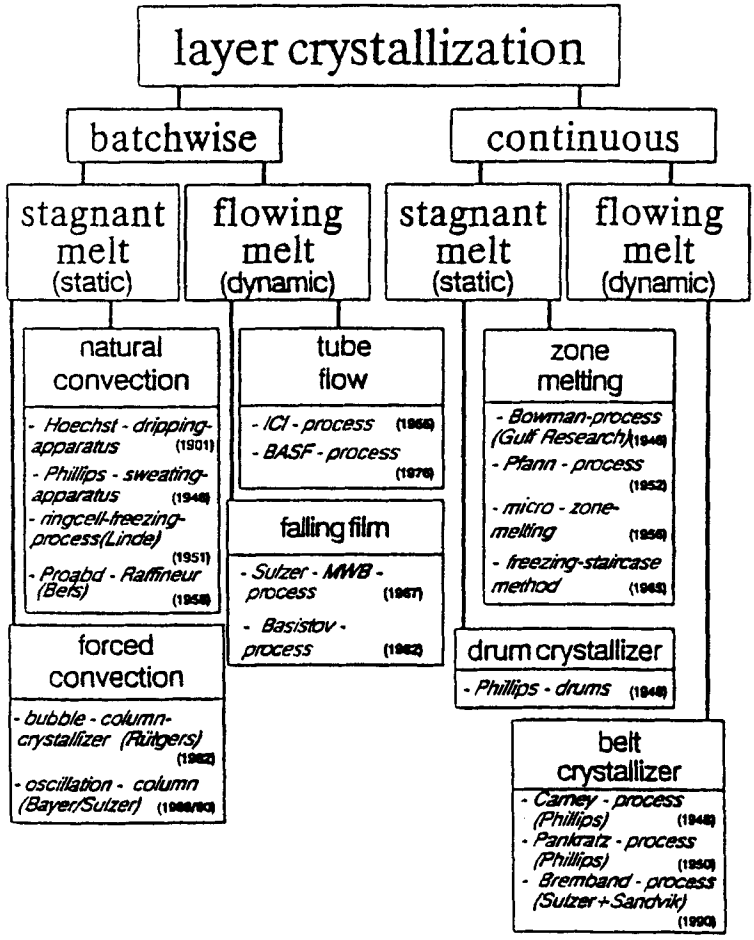

FIGURE 4: Layer crystallization [12]

The best known type of apparatus are the Hoechst "drip off apparatus" [17] and the Proabd Refiner [18] schematically shown in Figures 6 and 7 (see also [19]).

In both processes the melt to be separated is filled in heat exchangers with tubes or plates and subsequently crystallized by lowering the temperature. When crystallization proceeds, e.g. two hours for the purification of benzoeic acid and 30 hours for

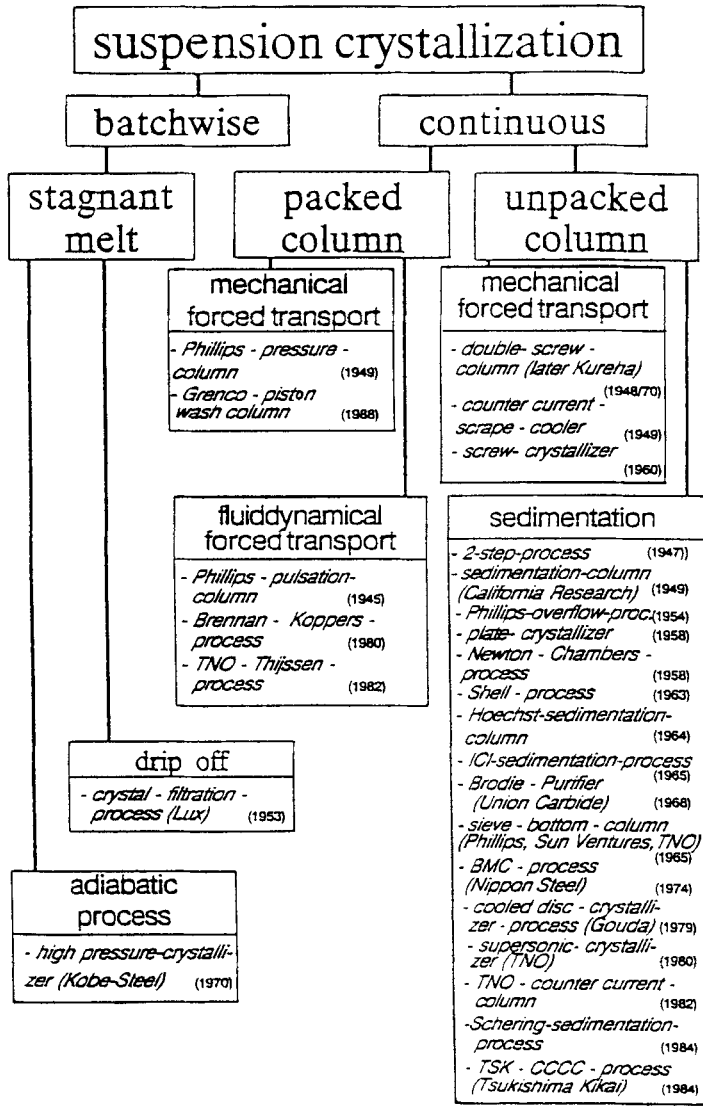

FIGURE 5: Suspension crystallization [12]

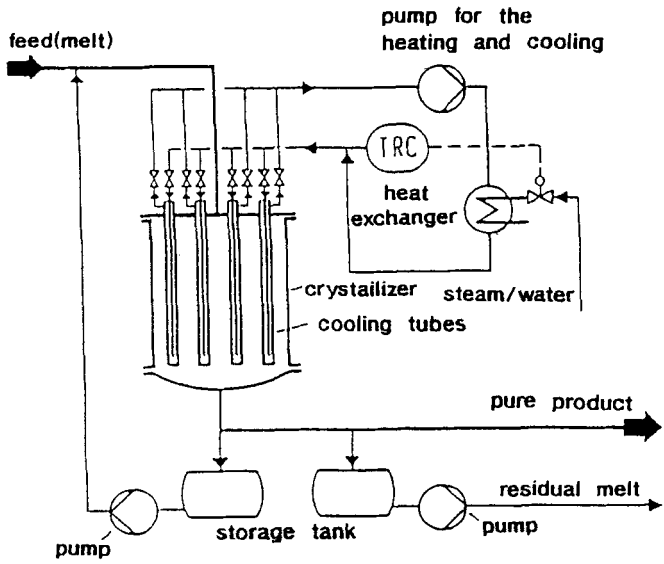

FIGURE 6: The Hoechst process [19]

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monochloracetic acid, the remaining melt becomes more and more impure. At the end of the process the residual melt, highly enriched with impurities, is allowed to drain through an opening at the bottom of the apparatus. The product is recovered by melting the crystals held back in the crystallizer and collecting the melt in a different tank than the residue.

A film of highly contaminated melt of residue composition will be retained on the crystal surface and influence final crystal purity, unless removed prior to total melting. This film or at least most of it can be removed by post-crystallization treatments like washing or sweating (see section 4) [6,19].

Since in the described processes the heat- and mass-transfer towards the separating surfaces only happens by natural convection, the volume-time-yield is relatively low. To improve the effectiveness of such a process Stolzenberg [20], Kuszlik [21] and Kehm [22] designed apparatus in which the melt is mixed by inert gas bubbles

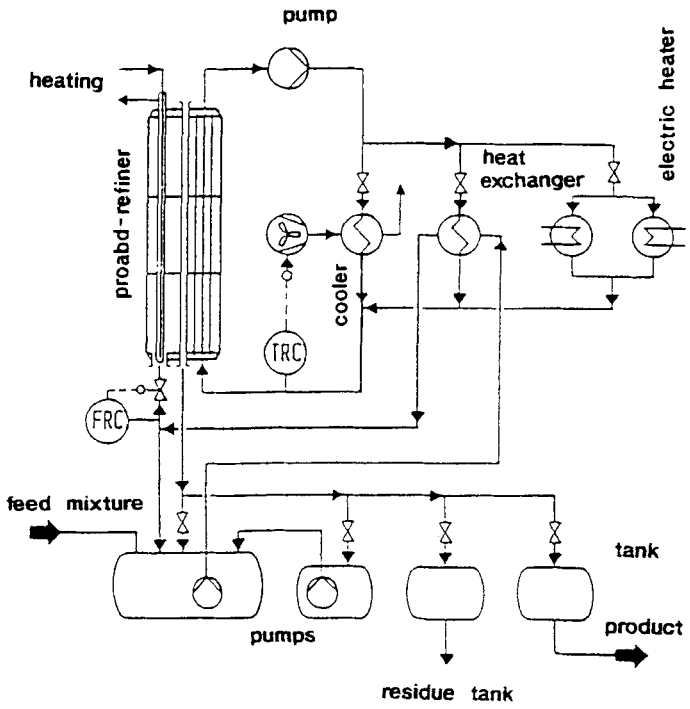

FIGURE 7: The Proabd process [19]

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(Figure 8) or pulsation (Figure 9), respectively, without any melt circulation. The aim of mixing in front of the boundary layer is to reduce the boundary layer thickness and therefore the concentration gradient.

A pulsation of melt helps to enhance the crystallization efficiency especially in cases where the impurity content in the feed is lowest. Ulrich et al. [24] and Kuszlik [21] demonstrated this by experiments.

With the equipment shown in Figure 9, Kuszlik investigated the difference between pulsed and static (stagnant melt) crystallization for different initial impurity concentrations (0 - 10 wt-%) and different process times (1 and 4 h) while the yields are kept constant to 75 %. In Figure 10 results are presented for the test systems ca-

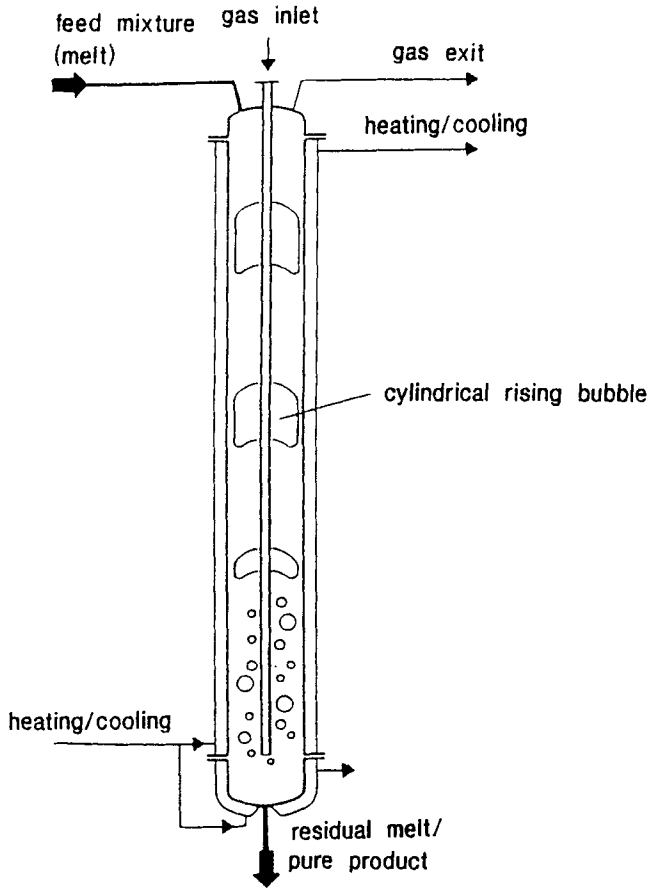

FIGURE 8: Bubble column crystallizer [19]

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prolactam/cyclohexanone and p/o-dichlorbenzene. The results are presented in the form that the separation factor K (equal to the effective distribution coefficient) is plotted against the average crystal growth rate.

For the crystallization of caprolactam/cyclohexanone (left diagram) the additional purification effect under pulsation is much lower for high initial impurity content.

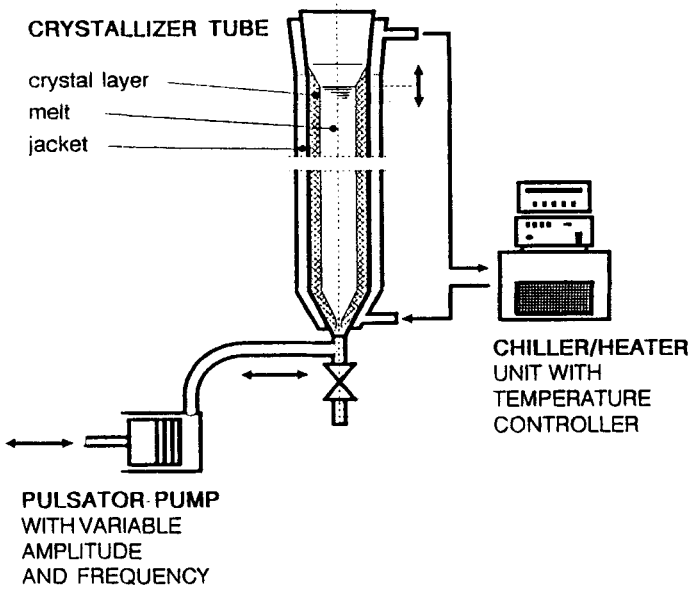


FIGURE 9: Pulsed crystallizer [21]

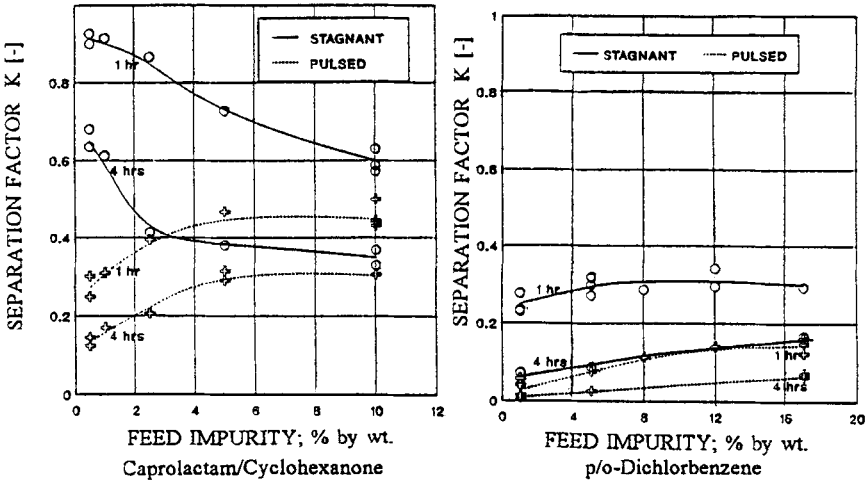


FIGURE 10: Dependence of the distribution coefficient on the initial impurity concentration and average growth rates in pulsed crystallization. Left: Caprolactam/Cyclohexanone; Right: p/o-DCB [21]

An explanation is that the impurity increases the viscosity of a mixture and therefore the mass transport is worsened. Thus, the pulsation is more effective with low initial impurity concentrations.

Generally the purification result is much better the lower the crystal growth rates. Since the yield is the same in all experiments (about 75 %) product purity increases as growth rates are reduced as to be seen in Figure 10.

For the system p/o-DCB the separations are better than for caprolactam because the viscosity of the mixture and therefore the Schmidt-number is much lower, too (Schmidt-number for caprolactam: 92150, for DCB: 376).

However, the decrease in impurity concentration when pulsation is added is greater for caprolactam. In practice it is easy to add a pulsation pump to an existing static crystallization unit. Pulsation should be applied preferably in the final stage, since the pulsation is most effective at these conditions, as seen in Figure 10.

3.2 DYNAMIC PROCESSES AND APPARATUS

Forced convection by circulating melt is the main characteristic of dynamic melt layer crystallization. The melt flows as a total stream or as a falling film through the inside of tubes that are cooled from the outside. Three well-known processes are: the Sulzer-Falling-Film- (Figure 11) [25], the ICI- [26] and the BASF-process [11].

In Figure 11 the flow scheme of the Sulzer-Falling-Film-process is shown.

Generally the melt coming from a feed tank is continuously circulated through the tubes of a tube bundle heat exchanger until the crystal layer is thick enough. The process is usually stopped when the optimum between the thickness of the layer, the yield, the energy and the time is reached. After the crystallization procedure, post-treatment of the crystal layer like sweating and washing can be conducted to improve the purity of the product (see section 4). If required, e.g. for the production of ultrapure substances, the processes can be performed in a multistage fashion. Multistage process requires only storage tanks as additional equipment, but more energy and longer production time cycles.

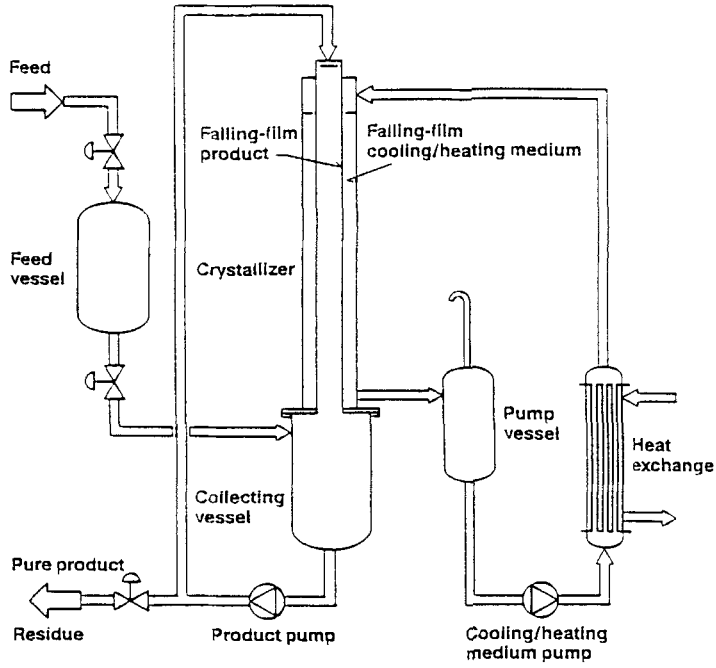


FIGURE 11: The Sulzer-Falling-Film- process [27]

(We thank the Sulzer Company to make the picture available for publication.)

While the BASF-process is recommended [11] for some products, e.g. for acrylic acid, adipic acid nitril and β-naphthol; the Sulzer-Falling-Film-process is used throughout the world for a variety of products. Some of them are benzoeic acid, pharmaceutical intermediates, caprolactam, dichlorbenzene, isocyanates and phenol [19].

The largest Sulzer-Falling-Film-equipment consists of 6 apparatuses with 1250 tubes and a standard tube height of 12 m. Each apparatus has a diameter of 4 m. Total production of 150 000 tons per year of a product with a purity in the parts per million range is achieved [28].

3.3 CONTINUOUS PLANTS

The main disadvantage of the static and dynamic solid layer techniques as described above is that they are batch-processes, but they deliver more consistent product than currently used continuous processes. In technical application deadtimes of charging and discharging and energy to heat and cool the equipment and the heat carrier are inevitable. To avoid deadtimes and to save energy continuous operating plants are preferred in the chemical process industry. Problems in running continuous plants are the handling solid transport and the solid liquid separation.

The simplest continuous approach is a drum cooler. These are often introduced in cascades to serve as continuous countercurrent purification processes. Chaty and O'Hern [29] and Gelperin et al. [30] proposed them for the purification of naphthalene and Graham [31] for benzene.

An approach to avoid the mentioned problems and integrate sweating and washing processes leads to a belt-crystallizer (see Figure 12) introduced by Ulrich et al. [32]. The invention relies upon a conveyer manufactured from stainless steel positioned at an angle and being cooled from the bottom.

Crystallized material is transported to the upper end of the steel belt while the residue flows down over already crystallized product. By using different cooling or heating zones on the belt, sweating and washing operations can be integrated into one apparatus.

First obtained results are presented by Hünken et al. [34,35,36]. These results suggest that in the continuous Bremband process the product mass flow rate will be larger and the energy consumption will be much lower than in batchwise working processes, e.g. in comparison with the Sulzer-Falling-Film-process. Additionally it is possible to obtain a purification efficiency which is better than one Sulzer crystallization stage. Results gained in one countercurrent crystallization step for the separation of isomers (p/m-DCB, with an impurity concentration of 5 wt-% m-DCB) are compared with results of the one crystallization cycle of the Sulzer-process in Figure 13/14 and 15.

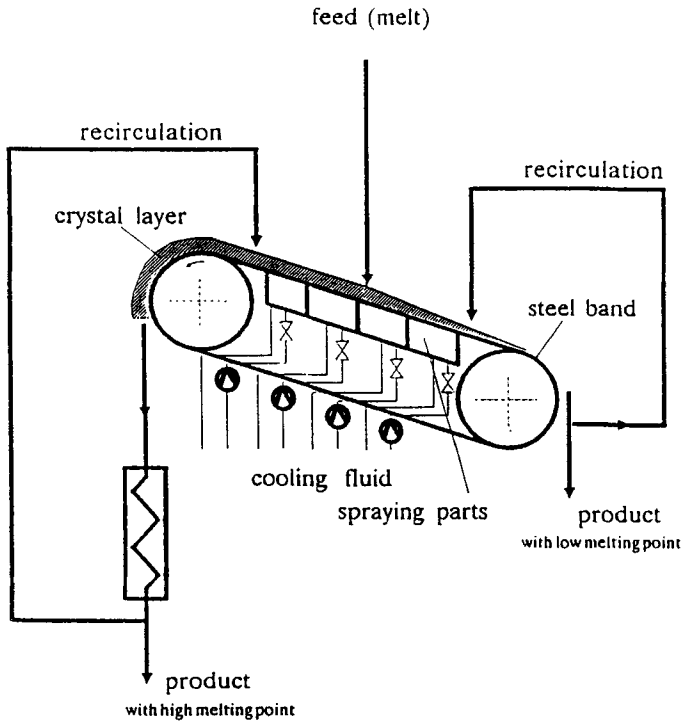


FIGURE 12: The Bremband process [12]

In Figure 13 the effective distribution coefficient is shown versus the crystal growth rate. The effective distribution coefficient reached with the continuous process are in the same range with the Sulzer results. The Bremband process enables crystallization with higher crystal growth rates or in shorter retention time, respectively. In that sense the countercurrent crystallization process is 1,5 times more effective, although the Reynold's number of the melt in the batchwise working process is much higher than in the continuous process.

Figure 14 shows the obtained mass flow rates per square metre cooled surface (m_{cr}) for the Bremband and Sulzer process as a function of the crystal growth rate.

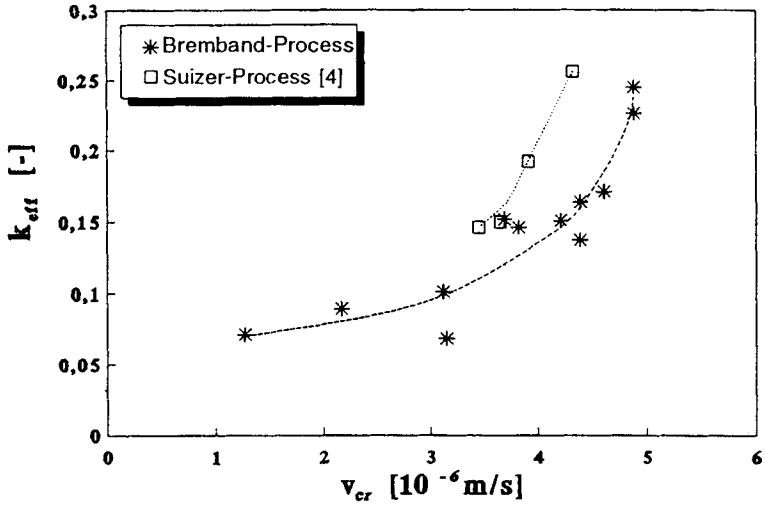


FIGURE 13: Comparison between the purification efficiency of the Bremband process and the one-staged Sulzer-Falling-Film-process. [35]

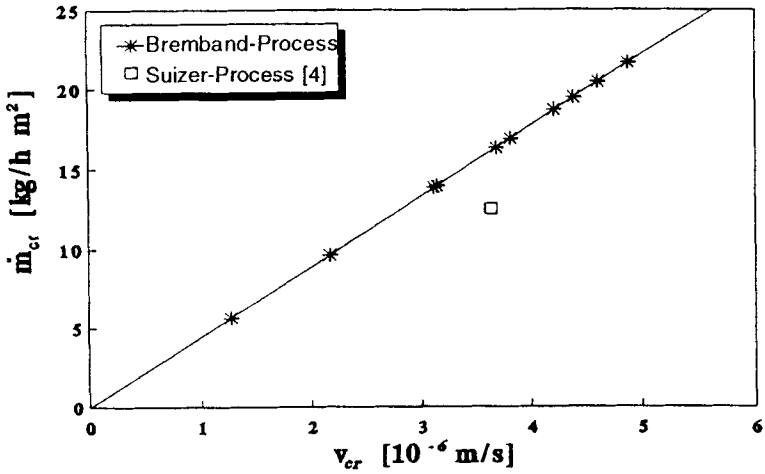


FIGURE 14: Mass flow rate versus growth rate [35]

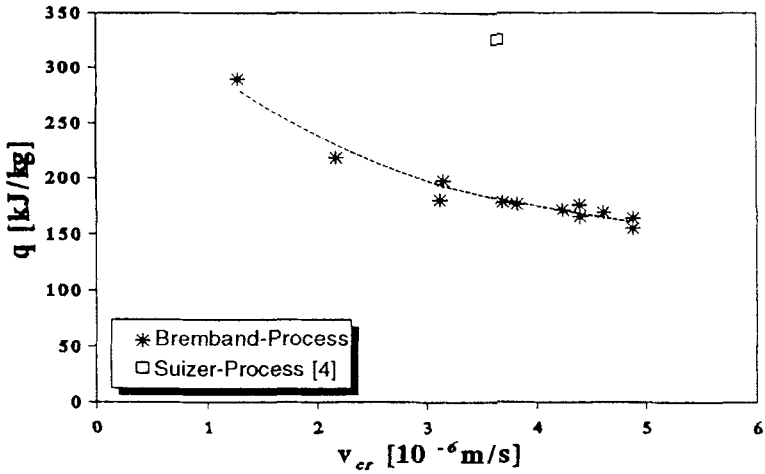


FIGURE 15: Energy consumption for the continuous Bremband and the discontinuous Sulzer-Falling-Film-process [35]

The mass flow rate of the crystals is a linear function of the crystal growth rate. For a crystal growth rate of nearly 4 * 10^{-6} [m/s] the mass flow rate of the Bremband process is 1,3 times larger than in the Sulzer process. The higher mass flow rate is possible because no dead time for charging, discharging and remelting is needed. Energy consumption per crystallization cycle and equal crystal growth rates for the processes are compared in Figure 15.

As seen from Figure 15 the needed energy per kilogram product (q) and per crystallization cycle of the batchwise crystallization process is about 1,8 times larger than the belt process. Here it must be mentioned that the ratio product to feed has been between 0,005 and 0,02 for the Bremband (without recirculation) and about 0,5 and 0,7 for the Sulzer process, respectively. Additionally the energy consumption per kilogram product for the batchwise process is much higher due to the cooling and heating of the whole apparatus and the heat carrier media in each crystallization stage.

Finally, it should be mentioned that the scale-up of the Sulzer-process is simple, since it is only necessary to increase the number of tubes (see section 3.2). In case of the Bremband-process production capacity is limited by the width and the length of the steel belt. 10 metre in length and 6 metre in width seem, however, not to be a problem. Further scale-up needs further study of the equipment.

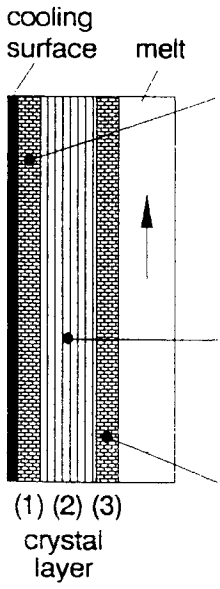
4. Sweating and Washing Steps

In the process of melt layer crystallization there are three phases in which impurities can be trapped in the solid layer:

1. nucleation (initiation step)
2. crystallization (solid layer growth)
3. end of crystallization (draining of the residual melt).

These phases determine the efficiency of the crystallization process with regard to purity. While controlled nucleation and crystal growth leads to a relatively pure layer, supplementary operations like sweating or washing are conducted to improve the separation result. Additional operations involve a product loss or contamination of already purified material, however, with less energy and in shorter time and better yields than an additional crystallization step. In Figure 16 a crystal layer with its potential positions of impurity inclusions is shown. Reasons for inclusions and methods to avoid or to reduce inclusions have been described previously.

In the nucleation phase when high supercoolings are present many nuclei form rapidly on the cooled surface so that impure melt is included in the layer. Dendritic growth of nuclei can be prevented by a seeding procedure or by controlled nucleation. It is therefore necessary to control temperature of the cooled surface by temperature programs or to control the flow rate of the feed stock in front of the cooled surface.



Step	mechanisms of impurity incorporation	measures to prevent impurities in the crystal product	additional purification measures
(1)	high impurity concentration due to nucleation at high supercooling	- nucleation by controlled temperature and flow conditions - controlled seeding - mechanically induced nucleation by: - shock waves - ultrasonic vibration - cavitation	- sweating
(2)	impurities in the crystal layer on account of high crystal growth rates	"criterion of purity" relates the maximum allowable growth rate for the production of a pure layer to the relevant set of flow conditions	- sweating
(3)	impurities due to adherance of contaminated residual melt at the end of the process	minimized and smooth crystal layer surface to reduce the wettable area	- sweating - washing

FIGURE 16: Mechanisms of impurity inclusions and methods to inhibit inclusions [37].

During crystal growth liquid inclusions of highly contaminated melt will be entrapped in the layer if the growth rates are too high. To avoid this kind of contamination the so-called purity criteria have to be considered (see section 5).

The adhering of highly contaminated residual melt on the crystal layer at the end of the crystallization process is the last form of possible layer impurities. It reaches a minimum when the crystal layer surface is smooth and can be withdrawn by sweating or washing.

All mentioned impurities of the layer can be extensively removed by additional purification steps which will be presented in the following.

4.1 DEFINITIONS

The sweating process is a temperature induced purification step. After a crystallization process the temperature of the cooling surface is raised to about the melting point of the pure crystals. Due to the lower melting temperature the contaminated melt will drain out of the pores of the crystalline layer. This process is helped by a decrease of the viscosity due to the higher temperature.

The washing process can be divided into rinsing and diffusion washing. If highly contaminated residual melt adhering to the crystal layer is substituted in a few seconds by a purer washing fluid then the process is called rinsing.
If the washing liquid is present in front of the crystal layer for 15 to 20 minutes or longer then liquid with higher impurity concentration diffuses out of the pores into the washing fluid in a measurable amount. To avoid the crystallization of the washing liquid onto the crystal layer it must be superheated. Therefore the warm washing liquid introduces simultaneously a sweating from the liquid side which increases the efficiency of the washing step. Both phenomena - diffusion and sweating from the liquid side - are included in the so-called diffusion washing.
The efficiency of the post-treatment depends, as well as the crystallization process, on the properties of the crystal layer (purity and smoothness) and on the chosen process type. Parameters to consider, especially for the washing procedure, are purity, temperature, amount and flow regime of the washing liquid [16, 39].

4.2 EXAMPLES

Neumann [40, 41] compared the efficiency of static and dynamic crystallization by using the test systems caprolactam/cyclohexanone and naphthalene/biphenyl. He used a tube crystallizer with falling film device (Figure 17) and investigated the crystal growth rates for different impurity concentrations (1, 5 and 10 wt%) and the efficiency of the sweating and the diffusion washing step (Figures 18/19/20).

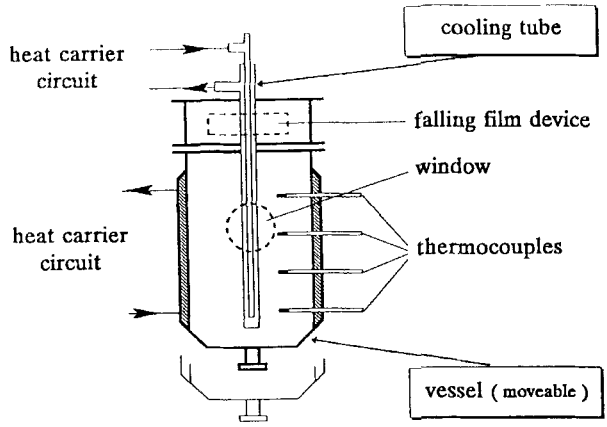


FIGURE 17: Tube crystallizer with falling film device [40]

The test unit consists of a cooling tube with a falling film device and a vessel that contains the liquid melt. Temperatures of the tube and the melt are separately controlled by heat carrier circuits. The cooling tube is equipped with a device to create a falling film for dynamic experiments.

In static case the cooling tube is positioned in the stagnant melt fitted into the vessel. The melt temperature is kept constant 1 to 2 °C above the equilibrium temperature during the whole crystallization process. When a temperature of the cooling tube of 1 °C below the equilibrium temperature of the melt is reached, the defined cooling program for the tube is started. The temperature of the cooling tube is lowered until the crystal layer has reached a thickness of 4 mm. Finally the tube with the crystal layer is removed from the melt and the adhering residual liquid drained off. Crystal product will be recovered by remelting it.

For the sweating step the temperature of the cooling tube is raised to 1 to 2 °C below the equilibrium temperature of the melt and kept constant for a defined time before remelting the product.

During diffusion washing the crystal layer remains inside the warm melt after crystallization while the temperature of the cooling tube is constantly at that tempe-

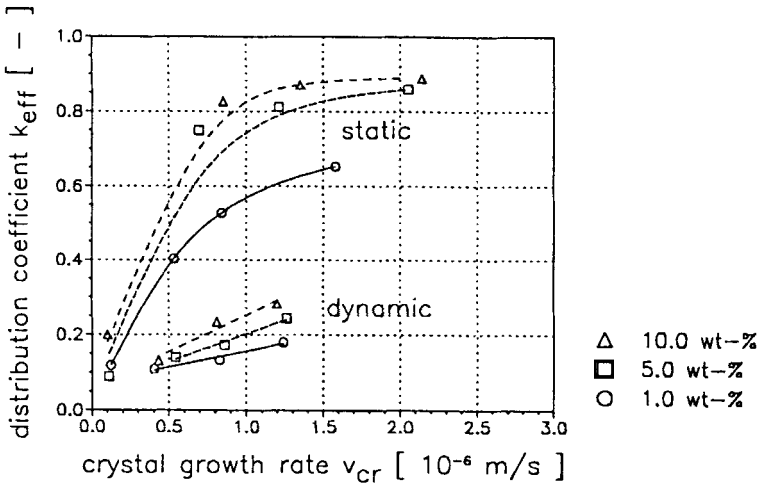


FIGURE 18: Comparison between static/dynamic crystallization [40]

rature reached at the end of the crystallization step. After a defined diffusion time the crystal layer is removed from the melt and remelted.

In dynamic experiments the vessel is only used as storage tank and the melt, circulated by a pump, flows over the tube surface in the turbulent flow regime. To avoid solidification of the melt in the falling film device, its temperature is kept constant 4 °C above the equilibrium temperature during crystallization.

The sweating step, applied after dynamic crystallization, is carried out in the same manner as in the static case.

For diffusion washing the melt is pumped continuously over the crystal surface while the temperature of the cooled tube is kept constant on its reached end temperature.

In Figure 18 results with caprolactam/cyclohexanone are presented. The obtained effective distribution coefficients of static and dynamic experiments are plotted versus the investigated crystal growth rates.

For a crystal growth rate of $0{,}5*10^{-6}$ m/s the static purification of a 1 wt-% impure melt is equivalent to $k_{eff} = 0{,}4$. The dynamic process under the same conditions

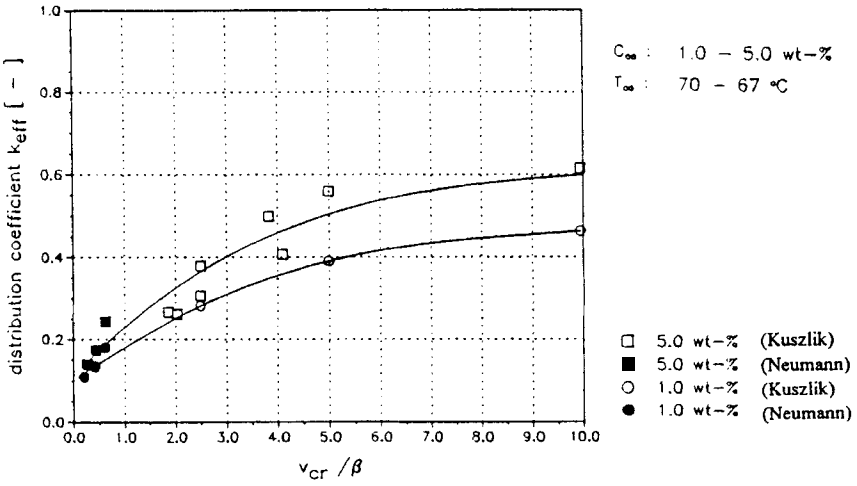


FIGURE 19: Comparison of two different dynamic processes [40]

achieves a purification efficiency of k_{eff} = 0,1. The improvement in the purification efficiency for the dynamic case amounts to more than 75 %. For higher impurity concentrations and higher crystal growth rates, e.g. $1{,}3*10^{-6}$ m/s, 60 % better purification with the dynamic process is still achievable.

Generally the dynamic process shows a much better purification efficiency than the static process. In order to obtain similar purification efficiencies with the static process the crystal growth rate has to be reduced by a factor of four. Lower crystal growth rates require, however, longer retention times.

In Figure 19 crystallization results of dynamic and pulsed experiments with caprolactam/cyclohexanone (1 to 5 wt-% cyclohexanone as initial impurities) are compared. Neumann [40] obtained the dynamic results with the test unit shown in Figure 17. Results of pulsed crystallization were carried out with the pulsed crystallizer shown in Figure 9 by Kuszlik [21].

In Figure 19 the effective distribution coefficient is shown versus the ratio of crystal growth rate (v_{cr}) and mass transfer coefficient (k). Although different parameters were chosen for the two different dynamic processes applied (both with turbulent

flow regime), the measured points fit very well with two curves. The curves support the statement that the purification becomes better with a lower ratio of v_{cr}/k (see chapter 5).

Neumann [40,41] stated that through sweating the purity can be improved by 15 to 30 % in the case of caprolactam and about 40 to 60 % for naphthalene (see Figure 20). In general the sweating effect increases with the initial impurity concentration before sweating, i.e. for a faster grown crystal layer.

By diffusion washing the purification result can be improved from 15 to 50 % for the caprolactam/cyclohexanone system and about 20 to 75 % for the naphthalene/-biphenyl system. In Figure 20 the results of dynamic crystallization without and with applied sweating and diffusion washing step for the system naphthalene/biphenyl (1 wt-% biphenyl) are presented. The starting condition for the additional purification step was a dynamically grown crystal layer produced with a defined cooling rate. Crystal growth rates were ranging from 0,5 to 3,5 * 10^{-6} [m/s]. The melt temperature has been 81 °C in all experiments. Such layers were grown as mentioned above for different crystal growth rates and the impurity concentration of each layer was analysed. The effective distribution coefficients obtained in crystallization experiments with applied sweating or diffusion washing step in comparison with results obtained in the crystallization step are shown in Figure 20.

The dynamic experiments with an initial impurity concentration of 1 wt-% lead to distribution coefficients about 0,2 at a crystal growth rate of 2,5*10^{-6} m/s. With an additional sweating operation, or a diffusion washing step, the layer purity can be improved and effective distribution coefficients of about 0,06 can be obtained.

For lower crystal growth rates and therefore purer crystal layers the efficiency of the post-treatment steps is reduced.

Wangnick [16] investigated the efficiency of post-treatments for the systems p/o-DCB and caprolactam/cyclohexanone. She used a tube crystallizer in which static (stat) and dynamic (dyn) crystallization (cr) experiments as well as post-treatments - sweating (sw), rinsing (ri) and diffusion washing (diff) - can be performed. One main conclusion of her work is that the efficiency of the sweating step depends,

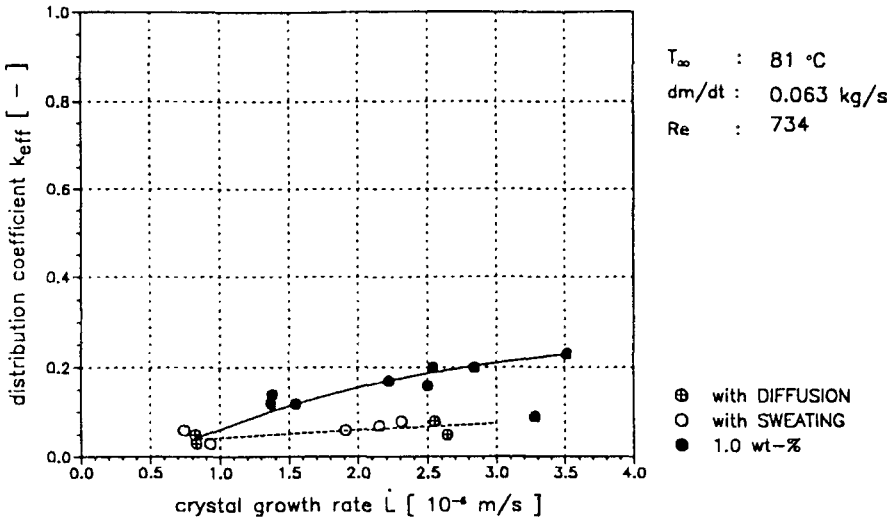


FIGURE 20: Results of sweating and diffusion washing experiments with naphthalene/biphenyl [41]

besides on sweating time and temperature, also on the crystallization conditions before the post-treatments.

For her investigations she carried out various crystallization experiments under same conditions (same crystal growth rates and impurity concentrations of the melt) and added the different post-treatment steps to determine the purification effect of each step. The highest possible purification effect (overall purification effect) was ascertained by results of diffusion washing experiments because the improvement of layer purity by diffusion washing is a sum of purification by sweating, rinsing and diffusion (see section 4.1). Start from this overall purification effect, the portion of each single process step on the purification effect is shown in Figure 21.

In Figure 21 the first two bars describe the DCB-experiments, the further two the caprolactam-experiments. For p/o-DCB a total layer purification (all) of about 89 % in the dynamic case, and 77 % in the static case, are reached by crystallization and diffusion washing with forced circulated washing liquid (mov). Layer purity is

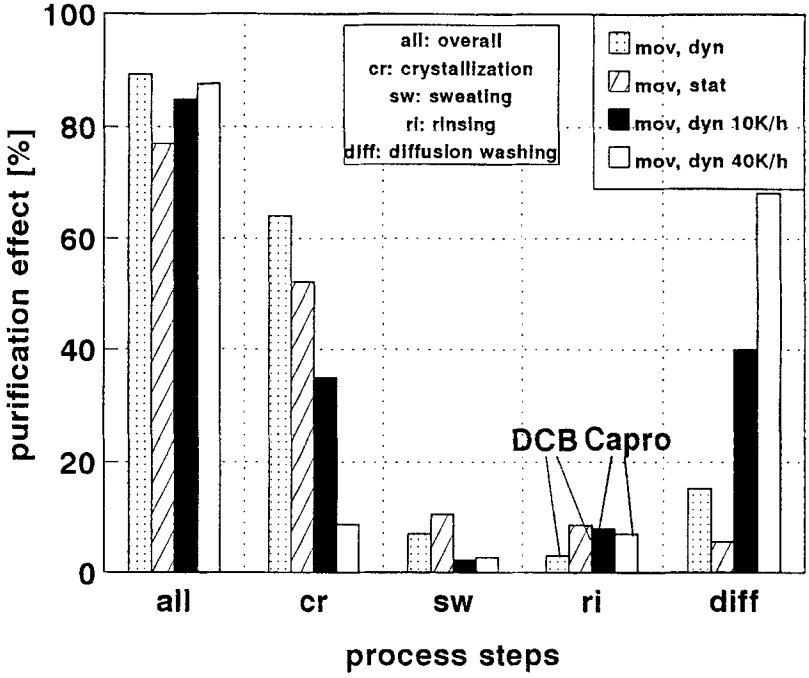


FIGURE 21: Share of the additional purification steps on the overall purification effect [16]

enhanced through sweating by 7 % and by 11 % of the overall purification efficiency. The portion of diffusion washing amounts to about 6 % and 15 %. The effect of rinsing contributes to the total purification by 6 % and 3 %, respectively.

The purification effect of the dynamic crystallization step for caprolactam/cyclohexanone is much better the smaller the cooling rates (10 and 40 K/h). Sweating and rinsing effects remain nearly constant (about 2 - 3 % for sweating and about 7 - 8 % for rinsing) for the different rates. Diffusion washing leads to a purity improvement between 40 % and 68 % for the lower and the higher cooling rate, respectively. Through crystallization a purification of about 35 % for a cooling rate of 10 K/h and of about 9 % for 40 K/h can be reached. The overall purification obtained

by crystallization and all post-treatments are about 85 % (40 K/h) and 87 % (10K/h), respectively.

Delannoy, et al. [42] investigated the purification of methacrylic acid from an industrial production with water as impurity present to about 1500 - 2000 ppm. Static and dynamic experiments have been performed on a tube crystallizer and the effective distribution coefficients before and after sweating have been compared. In static and in dynamic crystallization the process has been started with the equilibrium temperature of 16 °C. The cooling tube has been cooled down with constant rates ranging between 5 and 12 K/h in static crystallization and 30 and 120 K/h in dynamic crystallization. The flow regime for the falling film in dynamic crystallization has been turbulent with a Reynolds number of 480. After crystallization the mother liquor has been drained and the final product has been recovered by remelting the crystal layer. The sweating step has been performed by raising the temperature of the crystal layer after crystallization to the melting point of the pure product (15 °C).

In Figure 22 the effective distribution coefficient reached in static (left) and dynamic (right) experiments without and with added sweating step are shown versus the crystal growth rate.

For a crystal layer growth rate ranging between 0,3 and 1,7 $*10^{-6}$ m/s in static crystallization, the effective distribution coefficients ranged between 0,35 and 0,6 before and between 0,15 and 0,3 after sweating, respectively. The production rate of the static experiments is 75 wt-% of the total mass of the initial melt. Dynamic crystallization with crystal layer growth rates between 1 and 3,5 * 10^{-6} m/s leads to distribution coefficients ranging between 0,15 and 0,18. Through sweating the effective distribution coefficient can be reduced to values of 0,05 to 0,08. For an initial impurity concentration in the feed of 0,2 and 0,7 wt-% the distribution coefficient ranged between 0,15 and 0,2 before and 0,1 to 0,13 after sweating. In these experiments only an 8 wt-% yield could be reached. The limitation in the yields in the dynamic crystallization experiments is due to the experimental set up. With a different scale of equipment the same yields as in the static case can be produced

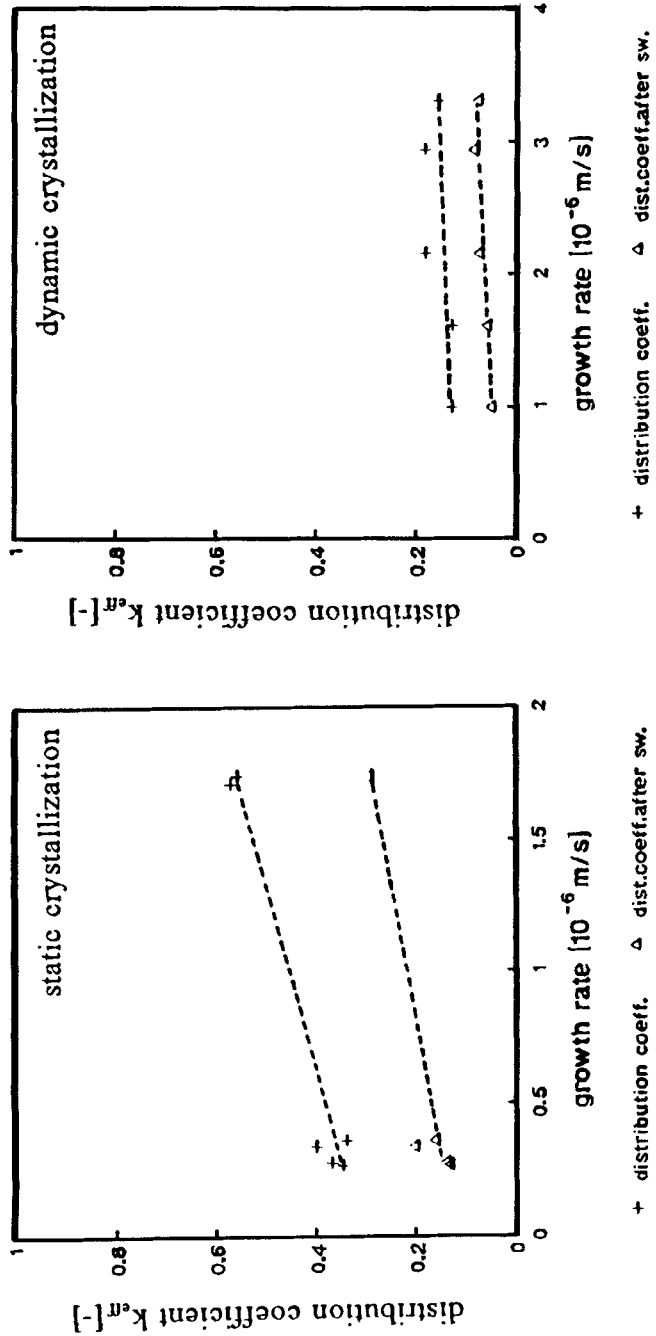


FIGURE 22: Static and dynamic crystallization and sweating results for methacrylic acid. Left: Static process; Right: Dynamic process. [42]

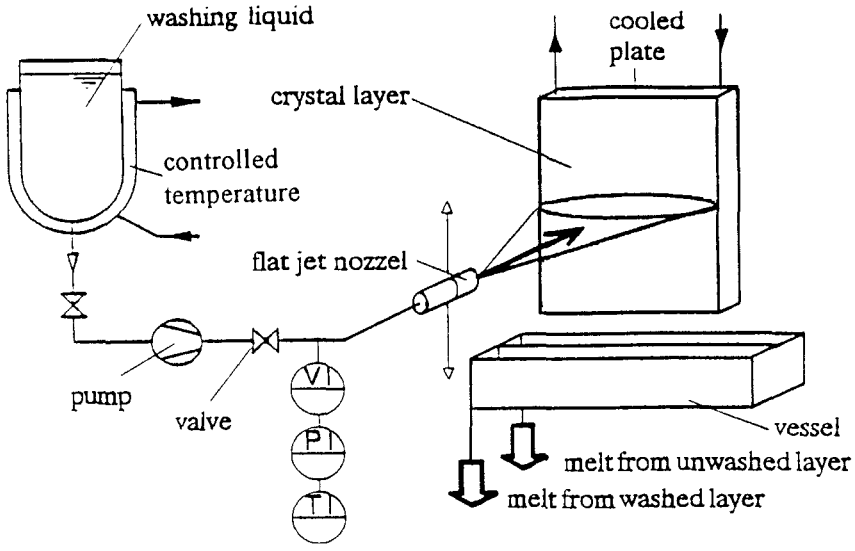


FIGURE 23: Rinsing of a crystal layer [43]

while retaining the purities shown here. The improvement in layer purity was achieved by sweating amounts of 42 and 50 % after static and about 33,3 and 44,4 % after dynamic crystallization. The sweating effect increases with increasing impurity concentration in the feed.

Poschmann et al. [43] used a plate like crystallizer (Figure 23) on which a crystal layer is grown on both sides of the plate to find the limiting conditions of the rinsing procedure.

Since the rinsing process has been carried out only on one side of the plate a direct evaluation of the post-purification step was possible. Ice was crystallized from aqueous salt solution and the rinsing was done with pure water.

The crystallization process was started by a seeding procedure. Therefore, the plate was covered with a thin layer of crystallized pure water. Afterwards the plate was introduced into the solution and cooled down at constant rates. When the crystal layer has reached the desired thickness of 3 mm, the plate was removed from

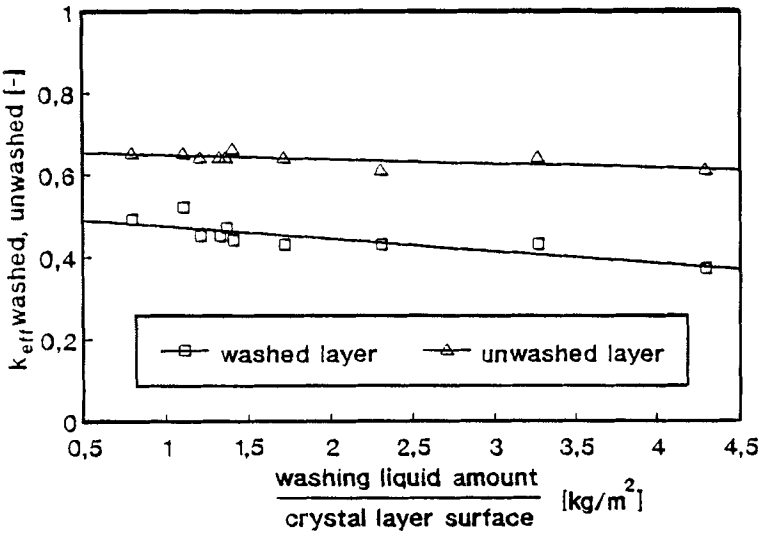


FIGURE 24: Effective distribution coefficient versus the amount of washing liquid [43]

solution. Washing liquid was pumped at controlled temperature from the vessel to the flat jet nozzle which was moved once during spraying parallel from the top to the bottom of the vertically fixed plate. The washing liquid was collected in a tray underneath the crystallization plate. The melt from each side was collected in separate vessels.

Among other parameters, the amount of sprayed washing liquid has been varied to determine its influence on the washing effect. Figure 24 presents results of the effective distribution coefficients versus the amount of sprayed liquid for the washed and the unwashed layers grown from stagnant melt with 10 wt-% salt.

The experiments showed that the resulting effective distribution coefficient after washing was between 10 and 20 % lower than those of the unwashed layers.

The amount of washing liquid ranged from 0,8 to 4,3 kg washing liquid per square metre crystal layer (or 0,2 to 1,2 times the mass of the crystal product) while the

mass of the crystallized product was kept unchanged. The temperature of the washing liquid was 17 °C.

Even small amounts of washing liquid are sufficient to remove significant amounts of adhering melt from the layer. The small further improvement of purity, reached with larger amounts of washing liquid, can be related to a warming of the outer area of the layer due to longer contact between the layer and the washing liquid. A partial melting of the layer takes place leading to a wash out of impurities inside such areas.

All examples presented elucidate that washing and sweating are important steps in improving the crystal layer purity after crystallization. Main advantages compared to a second crystallization step are:

Additional purification steps last only about one third or less of the needed time for a repeated crystallization step. Due to the shorter time and the fact that no phase change takes place lower energy is required than in a repeated crystallization step. Although the product loss amounts to about 10 %, the yield of pure product for sweating or washing, respectively, is higher than the purification by an additional crystallization step. An additional crystallization step recovers seldom more than 80 % of the feed as product.

5. Modeling of processes

Usually process design is based on theories, models and the experiences of experimental results (purity and quantity of the product) which in connection with a mathematical description of the process leads to the main process parameters. Such an approach is not possible in melt layer processes because of the lack of fundamental knowledge.

The aim of modeling a melt layer process is to simplify process design and allow the best technical solution at minimum cost. In general a high selectivity is reached when compact layers are crystallized. In such layers the part of the included and adhered residual melt is low with regard to the pure product.

It is known that the structure of a crystal layer mainly depends on the crystal growth rate (v_{cr}), the mass transfer coefficient (k) and the impurity concentration in the feed (c_∞). Usually the effective distribution coefficient k_{eff}, is defined as in equation (1). To predict the theoretical crystallization result two kinds of purity criteria are available: The v_{cr}/k-criterion [44, 45] and the gradients' criterion [46].

The v_{cr}/k-criterion is based on the boundary-layer-model for stagnant-films from Burton, Prim and Slichter [44], which relies only upon the mass transfer conditions and the concentration field to explain the separation effect in relation to the layer purity. The model was derived for the solidification of metallic systems with partly solid solubility. Starting from the diffusion-equation for the laminar boundary-layer, the authors showed that a functional connection exists between the equilibrium distribution coefficient k_0 and the effective distribution coefficient k_{eff}:

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0) \cdot \exp\left(\frac{v_{cr}\, \delta_c\, \rho_s}{D\, \rho_l}\right)} \quad . \tag{2}$$

Wintermantel [45] extended the equation while he substitutes the equilibrium distribution coefficient by the average concentration of one layer-element with liquid-inclusions:

$$k_{eff} = 1 - \frac{c_i - c_\infty}{c_\infty \cdot \left[\exp\left(\frac{v_{cr}}{k} \cdot \frac{\rho_s}{\rho_l}\right) - 1\right]} \quad . \tag{3}$$

Due to the unknown concentration at the interface the calculation of the effective distribution coefficient is not possible. Wintermantel demonstrated in experiments that the term in the denominator can be used for a uniform description of the distribution coefficient if there is a low influence of the temperature on the separation. Wintermantel [45], Kehm [22], Özoguz [12], Scholz [15] and Neumann [40]

investigated the applicability of equation (3) for many systems. With the uniform description a possibility to calculate and optimize commercial processes based on a few experiments is given.

In order to describe the whole separation process, besides the mass transfer, the heat transfer and the temperature gradient, respectively, have to be considered.

This is done by the gradient-criterion which postulates that dendritic crystal growth is always present if the real temperature profile in the boundary-layer has a steeper gradient than the melting point curve (constitutional supercooling, see Figure 2).

The mathematical description of the criterion is given by Rutter and Chalmers [46], who used the ratio of the gradients for the real temperature $\partial T/\partial x$ and the equilibrium temperature $\partial T_{eq}/\partial x$ at the boundary-layer as influencing variable:

$$\frac{\partial T_{eq}}{\partial x} = -m \cdot \frac{v_{cr}}{D} \cdot \frac{\rho_s}{\rho_l} \cdot \exp\left(\frac{v_{cr}}{k} \cdot \frac{\rho_s}{\rho_l}\right) \qquad (4)$$

$$\text{with} \quad \frac{\partial T}{\partial x} = \frac{\alpha}{\lambda} \cdot (T_i - T_{eq}) \quad .$$

If these gradients have identical values the limiting case is reached and no constitutional supercooling occurs.

For the production of pure crystals the real temperature gradient must be larger than the slope of the equilibrium temperature. The gradient-criterion represents therefore a limiting case from which no statements about the structure and the purity of the crystal layer can be concluded. The method enables formulation of the temperature control of the process to be made which in practice often leads to uneconomically low crystal growth rates [47].

The presented models for the description of the separation process are based on few characteristic parameters. They reduce the multitude of influencing parameters and show no correspondence between the parameter and the product purity. A prediction of the separation effect is not possible so that statements about possible applications in new fields presuppose experimental investigations.

Scholz [15] succeeded in finding a link between the two criteria and the product purity. For this purpose he evaluated the process data for the growth of pure crystals

according to the gradient-criterion and introduced them in the equation of the v_{cr}/k-criterion valid for the growth of pure crystal layers.

The analogy between heat- and mass transfer leads to an equation in which the ratio of v_{cr}/k for pure layer growth depends on the temperature difference ΔT between the temperature at the boundary layer T_i and the temperature in the feed T_∞:

$$\left(\frac{v_{cr}}{k}\right)_{k_{eff}=0} = 0{,}5 \cdot \frac{\rho_l}{\rho_s} \cdot \left(\sqrt{1 + 4\left(\frac{D}{a}\right)^n \cdot \frac{T_\infty - T_i}{m \cdot c_\infty}} - 1 \right) \quad . \tag{5}$$

In order to calculate the resulting layer composition, the unknown concentration at the interface c_i is empirically determined considering that the separation effect can be represented as a function of the dimensionless ratio of the average values of the growth rate and the mass transfer coefficient:

$$\overline{k_{eff}} = 1 - \frac{f\left(\overline{v_{cr}}/\overline{k}\right)}{c_\infty \left[\exp\left(\overline{v_{cr}}/\overline{k} \cdot \frac{\rho_s}{\rho_l}\right) - 1\right]}$$

$$\text{with} \quad f\left(\overline{v_{cr}}/\overline{k}\right) = f_0 \cdot \left(\frac{\overline{v_{cr}}/\overline{k}}{(v_{cr}/k)_{k_{eff}=0}} \right)^{n_{Subst.}} \tag{6}$$

$$f_0 = c_\infty \cdot \left(\exp\left(\left(\frac{v_{cr}}{k}\right)_{k_{eff}=0} \cdot \frac{\rho_s}{\rho_l} \right) - 1 \right) \quad .$$

$n_{Subst.}$ depends on the substance and has to be determined. From experiments with four different mixtures Scholz [15] found that the free parameter in his equation is a constant with a value of 2/3. For experimental checks of the free parameter he designed a cooled tube and a stirred vessel crystallizer. The results showed that for mixtures with Schmidt-numbers between 800 and 23000 the separation effect as a function of material properties and process parameters can be precalculated with the model. For example in Figure 25 the calculated results for the system naphthalene/-diphenyl are compared with experimental data by Wintermantel [48].

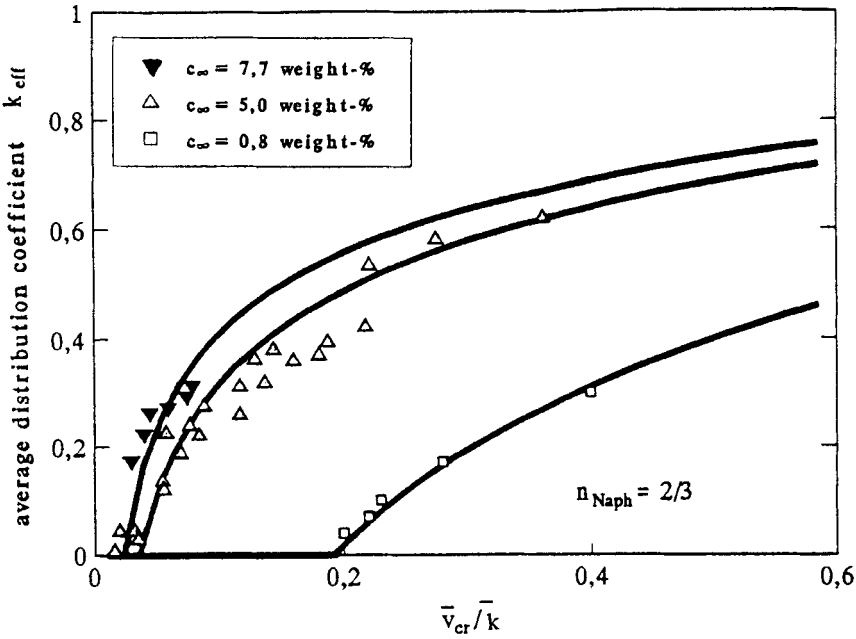


FIGURE 25: Comparison between calculated separation curves with literature data [15].

Wintermantel carried out his crystallization experiments in a tube crystallizer for different impurity concentrations of the melt. The temperature of the melt was kept constant 0,3 K above the equilibrium temperature.

In Figure 25 the average distribution coefficient is plotted versus the ratio of the average crystal growth rate and the average mass transport coefficient. The calculated results fit well the data obtained in the crystallization experiments. A low value of the ratio v_{cr}/k leads to a high purification effect, that is a low effective distribution coefficient. This means that the crystal layer will become more impure if v_{cr}/k increases. The point of intersection of the separation curve with the x-axis is shifted when different impurity concentrations of the melt are chosen. The value of $(v_{cr}/k)_{keff=0}$ decreases with increasing impurity concentrations. Since these trends are in agreement with the calculated data the model of Scholz [15] gives a good option to precalculate the separation effect without any experiments.

Wangnick et al. [16, 39] presented a model for the calculation of the purification efficiency of a solid layer melt crystallization process and the post-treatments. The authors describe the efficiency of each step by dimensionless numbers which result from a dimensional analysis of the influencing parameters.

As mentioned above the efficiency of a crystallization step can be characterized by the effective distribution coefficient. In order to describe the additional purification steps mathematically, the difference of the distribution coefficients of the crystal layer before and after each process is defined. For example, for sweating they define:

$$\Delta k_{eff,\,sw} = k_{eff,\,before\,sw} - k_{eff,\,after\,sw} = \frac{c_{cr} - c_{sw}}{c_{\infty}} = \frac{\Delta c_{sw}}{c_{\infty}} \quad . \tag{7}$$

In analogous manner such a value can be defined for rinsing and diffusion washing. The derivation of the dimensionless number for sweating is described in the following text. The other numbers were developed in similar ways.

Influencing parameters for the sweating process are the amount of liquid inclusions inside the crystal layer, their concentration and the sweating temperature. The dimensionless number (Π_{sw}) considers the former two influences by the effective distribution coefficient before sweating and after crystallization, respectively. The sweating temperature is normalized by the equilibrium temperature T_{eq} so that the dimensionless sweating number results as:

$$\Pi_{sw} = k_{eff,\,before\,sw} \cdot \frac{T_{sw}}{T_{eq}} \quad . \tag{8}$$

The dimensionless number is only valid under the condition of a constant sweating temperature just below the melting point of the crystalline phase and a sweating process that is driven until no more sweating liquid can be drained out.

To define a functional equation for the calculation of the difference of the effective distribution coefficients in dependence on the influencing parameters, the results of

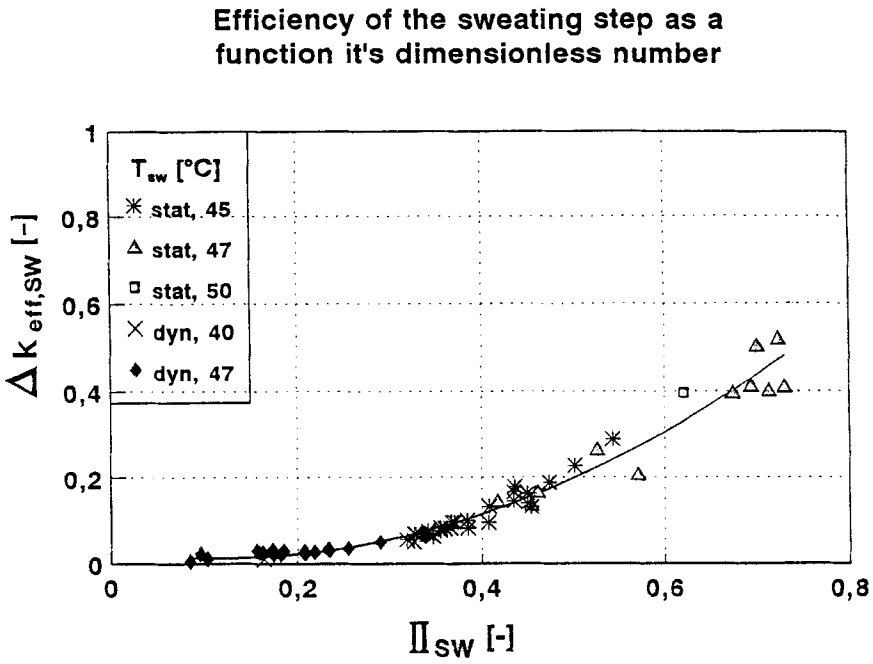


FIGURE 26: Differences of distribution coefficients for sweating experiments [16]

sweating experiments with statically (porous) and dynamically (compact) grown crystal layers of p/o-DCB (10 wt-% o-DCB) were compared with the model data. The experiments were carried out in a tube crystallizer with a cooling tube (50 mm outer diameter) positioned in a tempered jacket tube (70 mm inner diameter). For static experiments the annular space was filled with heated melt (ΔT_{eq} = 5 °C) and the temperature of the cooling tube was lowered. After a defined crystallization time the melt was drained and the crystal layer remelted. In dynamic experiments the melt was pumped from a tempered storage vessel over the cooling tube in laminar flow and lead back into the vessel. The starting temperature of the cooling tube was 50 °C for all experiments. The sweating of the crystal layer was induced by increasing the temperature of the cooling tube from 45 to 50 °C. The sweating liquor was

collected and analysed. The sweating ended when no more sweating liquid drained out of the pores. In Figure 26 $\Delta k_{eff,sw}$ is plotted versus the dimensionless sweating number, Π_{sw}.

The solid line describes the polynomial fit to the experimental data.

$$\Delta k_{eff,\,sw} = 0{,}028 - 0{,}277 \cdot \Pi_{sw} + 1{,}235 \cdot \Pi^2_{sw} \quad . \tag{9}$$

The efficiency of the whole solid layer crystallization process with all its additional purification steps can be calculated by the sum of the individual efficiencies of the retreatment steps:

$$k_{eff} = k_{eff,\,cr} - \Delta k_{eff,\,sw} - \Delta k_{eff,\,ri} - \Delta k_{eff,\,diff} \quad . \tag{10}$$

When the model of Scholz [15] enables the estimate of the purification efficiency of the crystallization step to be made without any experiments, Wangnick's research gives a first rate for the modeling of the post-crystallization steps. The task for the future is to extend the rate and derive a model for the precalculation of the whole crystallization process.

6. Symbols

a	stroke of the melt in the tube	[m]
a	thermal diffusivity	[m^2/s]
c	impurity concentration	[weight-%]
D	diffusion coefficient	[m^2/s]
f_0	constant	[-]
k	mass transfer coefficient	[m/s]
k_{eff}	effective distribution coefficient	[-]
k_0	equilibrium distribution coefficient	[-]
K	separation factor = k_{eff}	[-]
m	linearized gradient in phase diagram	[K/Gew%]
m	mass	[kg]
m_{cr}	crystal mass flow rate	[kg/h m^2]

n	exponent for the flow regime	[-]
$n_{substance}$	constant for the substance properties	[-]
q	ratio of energy to product mass	[kJ/kg]
T	temperature	[°C or K]
v	growth rate	[m/s]
x	radial direction	[m]
α	heat transfer coefficient	[W/m^2 K]
λ	thermal conductivity	[W/m K]
Π	dimensionless number	[-]
ρ	density	[kg/m^3]

Indices

all	overall purification effect	ri	rinsing
cr	crystal or crystallization	s	solid
diff	diffusion washing	sw	sweating
eq	equilibrium	∞	melt, feed
f	feed, melt		
i	boundary layer		
l	liquid		

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