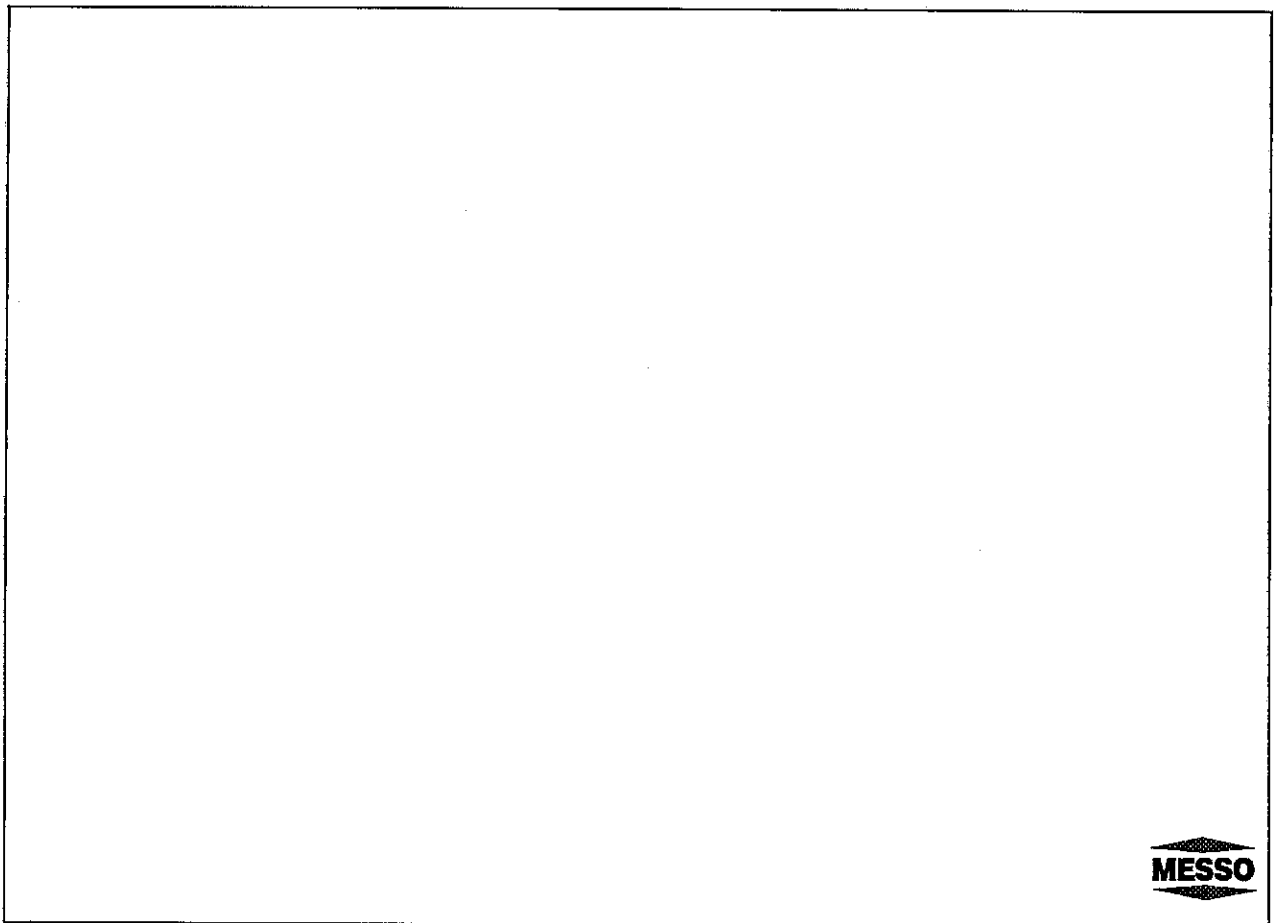


# Crystallization Theory in Practice

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### Abstract

The use and applicability of crystallization theories for industrial crystallization practice have been evaluated. The conclusion is that particularly plant users profit from the population balance model because it allows for bug diagnostics and prediction of response on altering conditions. Also for design purposes the available theoretical models greatly helped to increase insight in the wide range of events occurring in a crystallizer and how their interactions govern the resulting product. However, despite of the enormous amount of research work done so far, the quantitative application of theoretical models has not found entrance into the design of tailor-made crystallizers for strictly defined size distributions. From a designer's point of view further investments of time and money should be considered carefully because with the actual state of knowledge more than 80 % of the encountered problems already can be solved. One area of common interest that urgently deserves more attention in the near future is habit modification by additives.

### Introduction

Crystallization of salts from natural sources is nearly as old as mankind itself. From ancient times the need of crystalline goods has been steadily increasing (Fig. 1). Crystallization plants, however, have been built during the last hundred years. Research and development efforts in the area of crystallization with respect to industrial aspects started only about half a century ago.

Meanwhile, theories and models have been formulated and numerous single phenomena have been investigated. Compared to the theoretical insight thirty years ago - the time at which the Working Party on Crystallization was founded - it can be stated that at present the theoretical backgrounds of the unit operation crystallization are almost fully understood.

In the scope of an International Symposium like this the question arises how

valuable these theoretical developments have been for crystallization practice. Are crystallizers nowadays cheaper, more effective or simpler as they were in the past? What else is the use of the meanwhile available theoretical developments? Which role does theory of crystallization play in design and operation of crystallization plants and in which areas would further development be promising and economically justified?

In the scope of this contribution, we can only try to give indicative answers to these questions.

#### Crystallization in practice

A crystallization process is a complex plant for the production of an industrial bulk product. In the sequence of treatments, crystallization surely is an important but by far not the only unit operation. The feedstream often has to be purified, filtered or mixed in order to allow for chemical reaction prior to crystallization. After crystallization, the crystals have to be separated from the mother liquid, washed, dried and in particular cases other final treatments may be necessary. Storage and packing are often part of a crystallization plant. All these unit operations influence the properties of the crystallizate and have to be chosen and designed - without any crystallization theory - as careful as the crystallizer itself. Also secondary equipment like pumps, heat exchangers, vacuum equipment, process control devices and electrical power supply each play their role in the establishment of the final product.

With respect to the attainable crystal size it can be summarized (Fig. 2):

- With proper design of the crystallization and the unit operations prior to crystallization the crystal size can be influenced positively.
- All operations after crystallization influence the properties of the crystallizate in a negative sense. However, when designed correctly, product deterioration can be reduced to a minimum.
- All process steps in parallel to crystallization behave neutral when correctly chosen and designed. In case of non-optimal design a negative influence will be noted.

It will be obvious that certain demands are laid upon a crystallization plant that do not require the involvement of crystallization theory such as taking in account the peculiarities of slurry handling, optimal integration of all unit

operations within the plant, ensuring controllability and last but not least the right choice of construction material. The assured ability to meet production requirements with respect to quantity and quality is just as important as economical, simple and reliable operation of the entire crystallization plant.

The desired product can be the crystals as well as the mother liquid. If the desired product is the mother liquid the composition of the liquid directly determines the quality of the final product. In such a case easy solid/liquid separation is the only requirement with regard to crystals. A mean crystal diameter of 200  $\mu\text{m}$  is already sufficient to use simple centrifuges and can be obtained in most practical cases without problems.

When the crystallizate is being aimed at - which is mostly the case - the crystal size distribution can be an additional quality characteristic besides purity. However, requirements like a completely prescribed size distribution are by far not as common as it is generally being assumed. In many cases the required standards are derived from crystallizates already. Examples like sugar, salt, ammonium sulfate for fertilizers explain this statement. Here, requirements on crystal size and shape are not determined by particular applications but only by familiarity of the user with the product.

Therefore, only rarely crystallizers have to be tailor-made with respect to a particular size distribution. Consequently, the investment of manhours during crystallization plants engineering in such problems is accordingly low.

#### The practice of crystallizer design

One of the most important steps in crystallizer design is the collection, evaluation and examination of physical properties of the underlying system which are required for the process balance equations (solubilities, specific heats, thermal conductivities, viscosities). Such data can be found in the literature [1-4] or - in particular for multicomponent mixtures - have to be determined experimentally. If high product purity is required or when the outcome of process balance calculations requires experimental confirmation, laboratory scale crystallization experiments allowing for chemical/analytical examination - continuously, if the required information can only be obtained from continuous operation, else batch - are executed. Although crystallization kinetics is not the real aim of such investigations, proper planning and execution of such experiments also yields information about crystallization behaviour. It can be determined whether, compared with earlier experiences, crystallization is being influenced by components actu-

ally present in the mixture or whether the product is a rapidly growing or an easily-nucleating one.

For new or unknown product such tests should be generally performed also if product purity is not subject of investigation. However, also in this case kinetic data are not really determined.

If, from experience, no information about the metastable zone width or about settling velocities of the expected crystals in the actual mother liquid is available, experimental determination have to be performed.

Based on these data and on the required product size a crystallizer type has to be selected. As known from numerous publications [5-8], the available crystallizers can be divided into three classes:

- FC crystallizers (d 0,2 - 0,5 mm)
- DTB crystallizers (d 0,5 - 1,2 mm)
- Fluidized bed crystallizers (d 1,0 mm)

All these crystallizers are equipped with a forced circulation loop which serves to keep the content within the metastable zone limit in order to avoid primary nucleation. For the production of coarser crystallizates still using the forced circulation principle, additional effects are used to a different extent in the separate classes:

1. Reducing the pump tip speed to the level of what is hydraulically possible (FC- and DTB-crystallizers)
2. Reducing the specific energy input into the suspension via recirculation pumps (or stirrers) to a minimum, e.g. by separate suspension and heating flows (transfer from FC to DTB) or by complete elimination of the recirculation pump from suspension in order to prevent production of secondary nuclei as much as possible (transfer to fluidized bed crystallizer).
3. Installation of devices for fines removal/fines destruction and/or control of suspension density.

One could ask for an optimization of the - with respect to crystal size oppositely acting parameters - residence time and suspension density by correctly scaling up. A necessary condition for an in every respect successful scale up procedure for crystallization would be similarity in the conditions of geometry, kinetics and hydrodynamics. In crystallization, however, it is impossible to keep

all these conditions simultaneously constant. Mullin [9] stated already in 1961: "Scaling up of crystallization equipment is probably more difficult than that for any of the other unit operations of chemical engineering." Till now, no essential changes in this have taken place.

Griffith [10] (1947) formulated a "separation intensity" as a design criteria which is defined as the production rate of crystalline mass per unit crystallizer volume and per unit time (Fig. 3). From experimental data obtained from a wide range of crystallizer types and sizes and a wide range of substances he deduced that the values of the separation intensities - when recalculated for a standard product size - all lie in the same range. Only for fine crystallizates the S.I. factors have proven to be unreliable. In one of our own publications [11] in 1982 we defined a "specific production rate" for fluidized bed crystallizers, expressed as the weight of crystals produced per unit time and unit cross sectional area, as a function of upflow velocity and supersaturation (Fig. 4). Mersmann [12] showed 1989 for 17 systems from practical results that the maximum obtainable mean crystal size as a function of supersaturation each lies within a product typical narrow range (Fig. 5).

So, sophisticated complete scaling up from laboratory results is not yet possible and as shown, not necessary. Thanks to the now known theoretical relationships we are today more well-aimed in predicting crystallizer performance and concentrate, being aware of the uncompleteness of our knowledge, on comprehension of the essential single phenomena.

Typically an FC-crystallizer is designed for a crystal residence time of about 2 hours and a suspension density in the range of 15 - 25 mass%. This is mostly sufficient to yield a separable crystallizate. Increasing the residence time only results in marginal size increases, sometimes a size decrease may result due to the competition between crystal growth and crystal damage [13] (Fig. 6).

Sometimes the necessary residence time follows from the time required for equilibration. In such cases desupersaturation as function of time must be measured in the laboratory and taken as a basis for crystallizer lay-out.

When changing from one type of crystallizer to the other the altered geometry implies automatically longer residence times and reduced secondary nucleation. Both effects yield coarser product. For a DTB-crystallizer the residence time - because of geometric reasons - mostly amounts 3 - 4 h (Fig. 6). Suspension densities of 25

mass% can be well processed. Still the circulation pump in the DTB-crystallizer is the main source of secondary nucleation. Its flowrate is determined by the maximum allowable supersaturation (approx.  $0.5 \times \Delta c_{met}$ ) and is designed such that at constant specific energy input the rotational speed is as minimal as hydraulically possible. Calculation for a particular size distribution optimal rotational speed is neither possible nor necessary.

For a fluidized bed crystallizer, design criteria are the required circulation rate in order to remain within the maximum supersaturation limit together with the settling velocity of the smallest product crystal carried over into the heating loop. These values determine the crystallizer diameter and, together with a prescribed geometry, a minimum volume. Because of the variable suspension density and bed height the crystal residence time and hence the final product size can be adjusted over a wide range (Fig. 6). Also here a necessity for the application of crystal-lization theory does not exist for designing fluid-bed crystallizers.

Also fines destruction loops are generally designed in accordance with technical boundary conditions without taking kinetics into account. Dimensioning of the separation part is based on the settling velocity of the smallest carried over particles (mostly about 0.2 mm). The heat input in the fines destruction loop is - if this amount of heat has to be supplied additional to the thermodynamically required amount - determined rather by economical criteria. A flexible layout of the fines destruction loop provides an excellent means of tuning the product crystal size during plant operation.

#### Operation of crystallizers

For examination of practical operation and for the quantitative estimation of the effect of changed conditions on the resulting crystal size distribution, the calculation method using population balance theory has further established.

Based on an actual CSD produced under a particular set of conditions, the effect of changes in suspension density or production capacity, or from increasing or decreasing fines destruction can be predicted by calculation. In case control of crystallizer operation is required in order to produce a well-defined CSD in the entire range of throughputs, a process control strategy is required whose software includes crystallization theory. Although such a sophisticated control system is mostly unnecessary and hard to realize because of the long average statistical residence times in continuous processes, operation of modern batch crystal-

lizers can today be computer controlled by using theoretical considerations.

Summarizing evaluation of the importance of theoretical development  
for practical purposes

As has been shown the population balance and its derivatives have not found their entrance yet in numerical design of crystallizers.

However, the essential use of crystallization theory for design practice does not appear from quantitative applications of the models but from the model themselves (Fig. 7). The model allows for estimation of the effect of particular measures also without exact calculations. Developed and improved by the interactions between practitioners, who announced their problems and researchers who developed models, a tool resulted that also definitely took influences on the practice of crystallizer design. Also in those cases where the solution to a problem is not obvious at first sight, the design of crystallizers is much more reliable and robust as it was before thanks to the use of imaginary models. The importance of this statement is illustrated by bearing in mind that the three basic types of crystallizers are much older than population balance theory. Through population balance theory it became clear how these empirically developed crystallizers perform and how optimum operation can be achieved [7]. The question posed in the introduction "Are crystallizers nowadays cheaper and more effective as they were before?" - therefore has to be answered positively, thanks to crystallization theory.

In case further well-aimed research is performed the design of crystallizers for a particular size distribution regarding nucleation rate, attrition rate, growth rate and residence time as a function of equipment specific properties could be possible in a not too far future.

If, however, the industry would have to pay the costs for this research, a critical cost-yield analysis would lead to the decision the present tools and experience can solve more than 80 % of all the crystallization problems quite safely (Fig. 8). In certain cases process simulation of crystallizers is part of the scope of interest of plant users. Further research efforts in the direction of integration of all influencing factors - also hydrodynamics - in practice-related models would be useful.

A common point of interest of all parties involved is the request for research in the areas of structure of solutions of additives, more precisely, the revealance

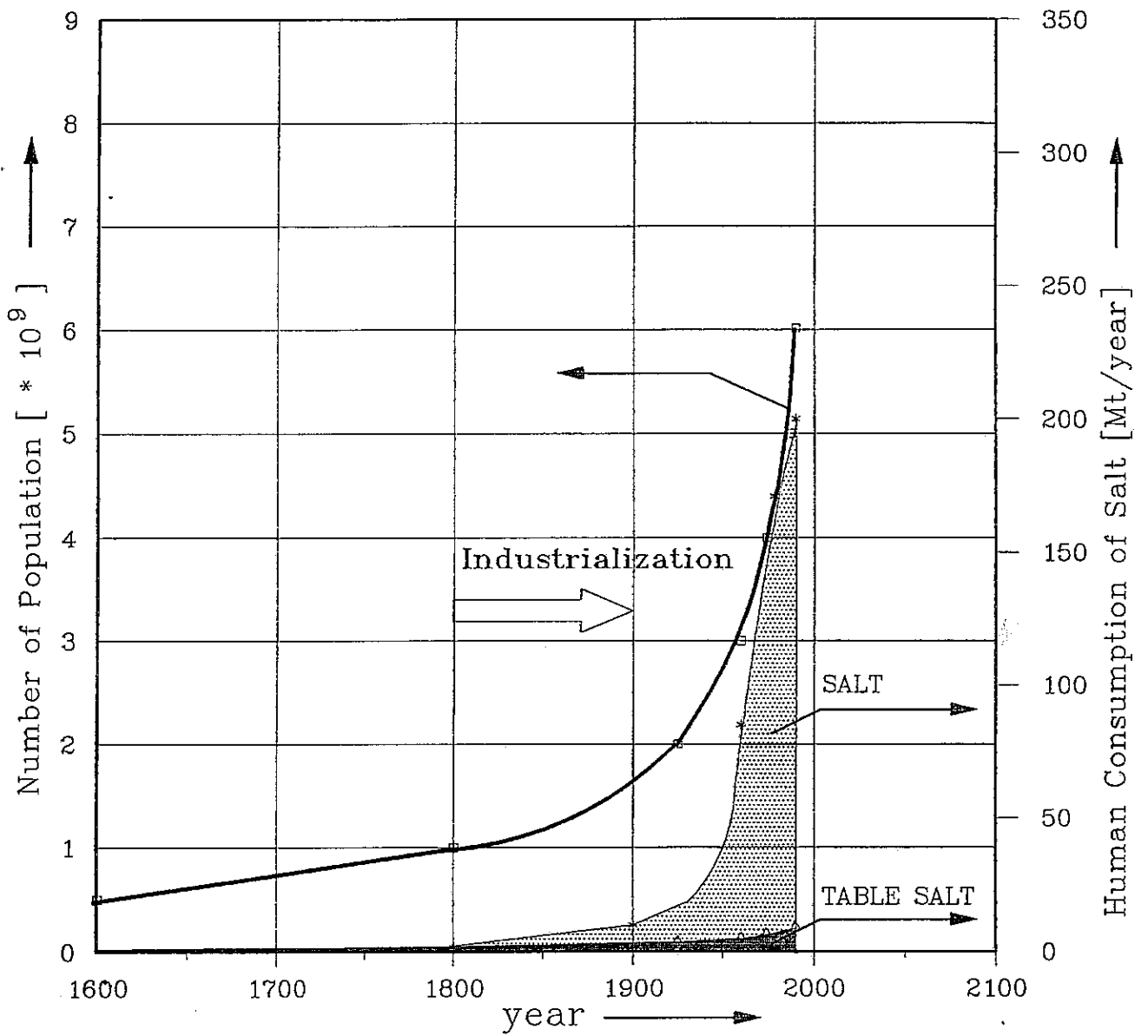
of mechanisms governing changes in kinetics induced by other components, be it in traces or dominating components [14]. The development of a screening method for aimed manipulation of the crystal habit or for recognition and elimination of changes induced by foreign components would be very helpful. Crystallizates that are hard to separate because of their needle or plate habit could hopefully be transferred into more compact particles by using the right additive. In this way the design of crystallization plants for difficult products could be simplified. In particular solid-liquid separation could be performed with simpler equipment, spending less on washing and yielding higher purity.

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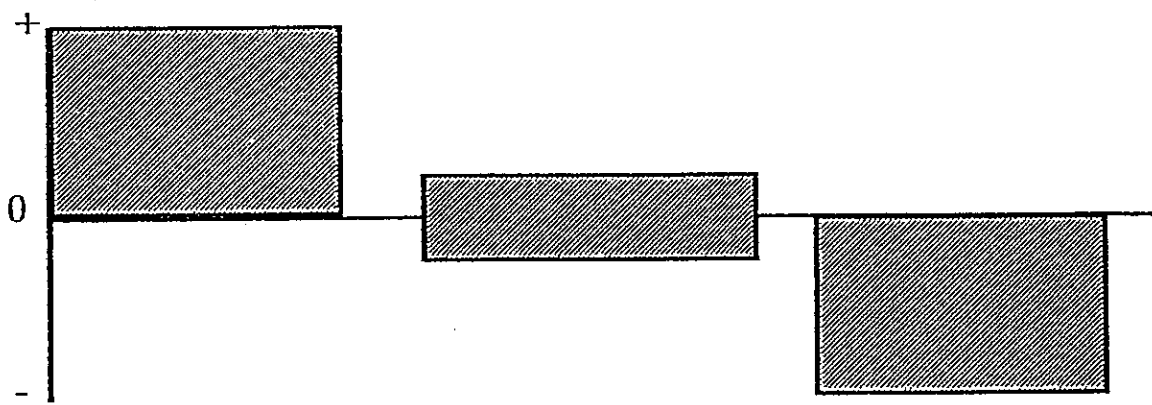
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GROWTH OF WORLD POPULATION AND  
TABLE SALT CONSUMPTION



PRE-TREATMENTS	PARALLEL TREATMENTS	POST-TREATMENTS
control of concentration filtration mixing reaction active carbon treatment	control and generation of: - vacuum - steam pressure control	slurry transport solid/liquid sep. drying packing

INFLUENCE:



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INFLUENCES OF ADDITIONAL UNIT OPERATIONS ON CRYSTAL QUALITY



Fig. 2

## SEPARATION INTENSITY FACTOR (Griffiths, 1947)

$$S.I. = \frac{L * P}{V}$$

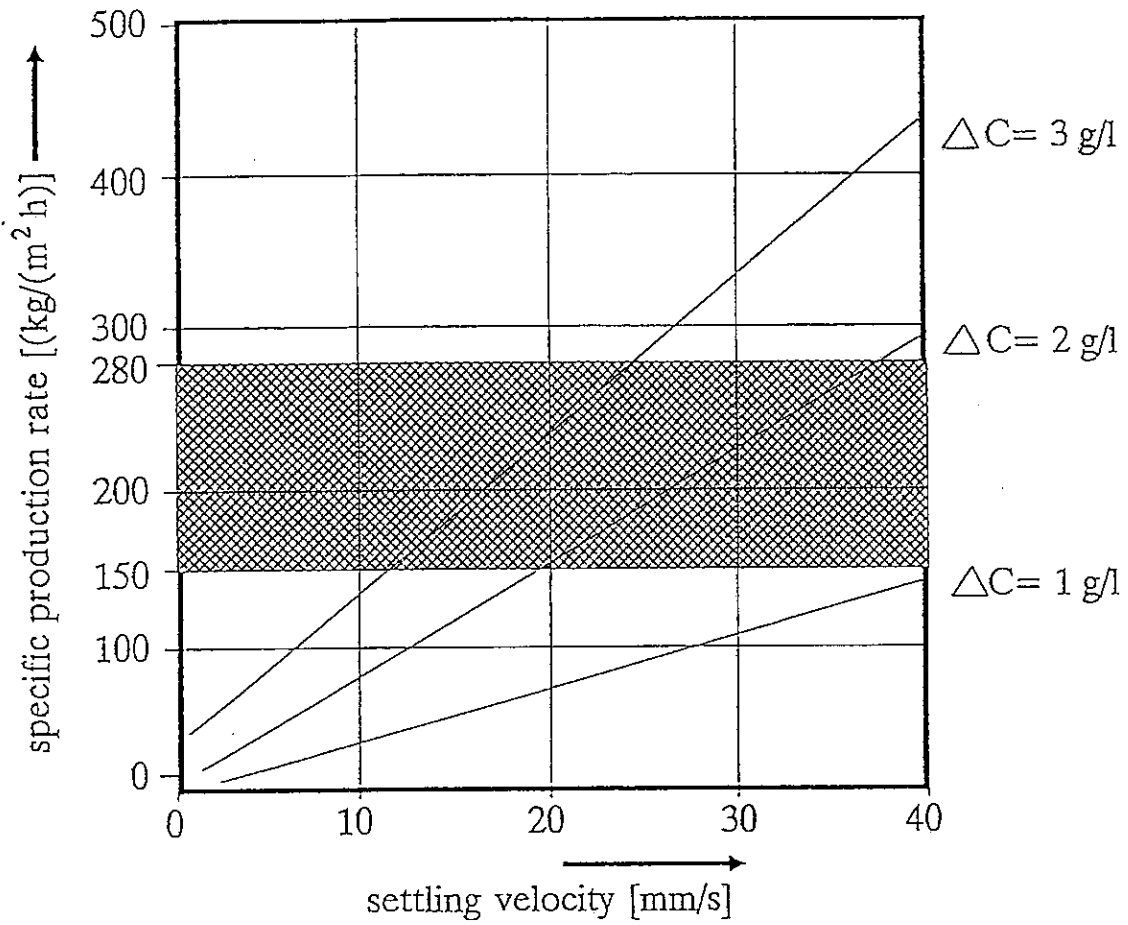
- $L$  = Relative product size [-]  
 $P$  = Production rate [kg/h]  
 $V$  = Suspension volume [m<sup>3</sup>]

Range : 50 - 300 kg/(m<sup>3</sup> h) for 1 mm equivalent crystals  
For room temperature 50, increasing to 300 at higher temperatures  
Applicability restricted to crystals > 1 mm.

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DEFINITION OF SEPARATION  
INTENSITY FACTOR

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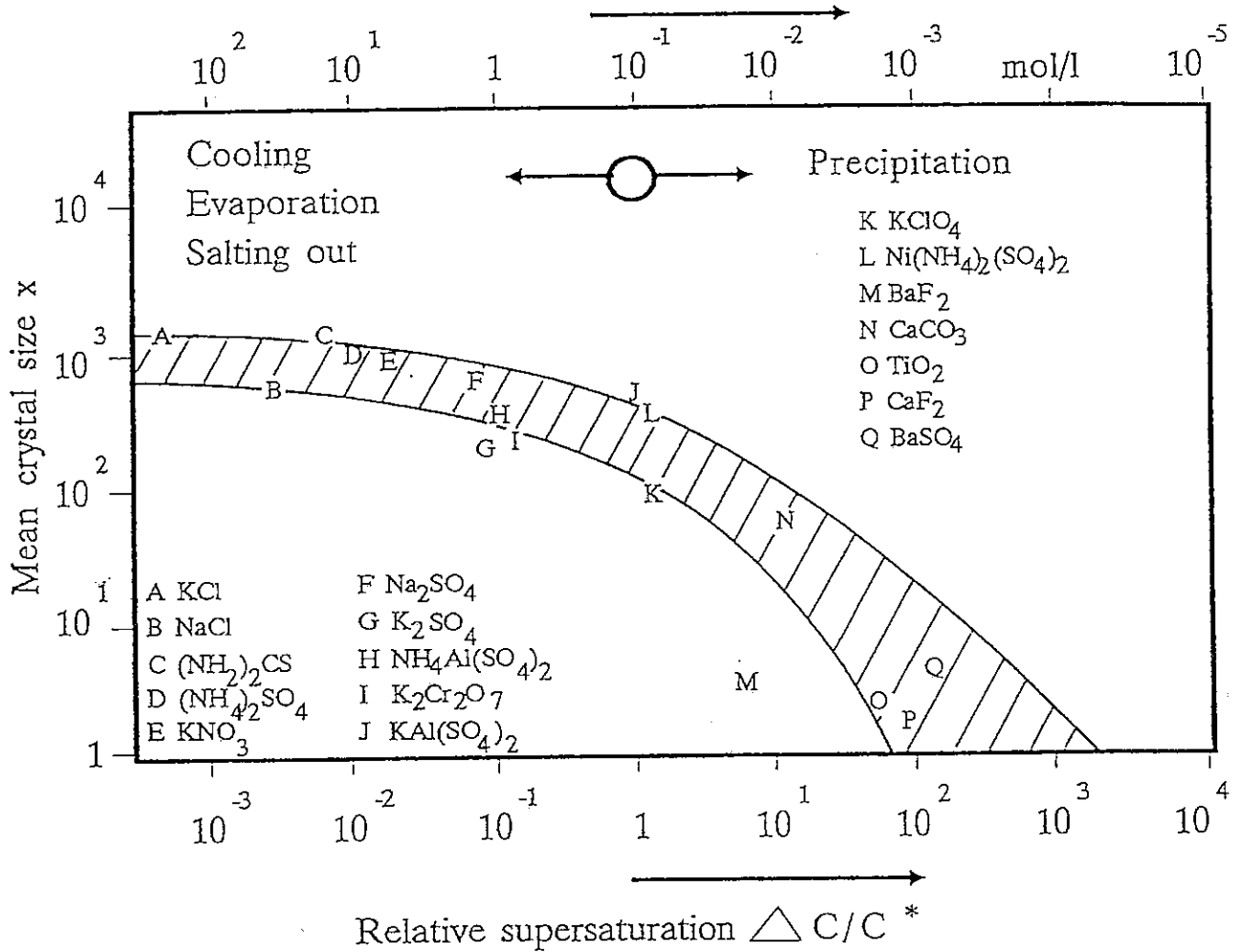
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SPECIFIC PRODUCTION RATE  
FOR OSLO - TYPE CRYSTALLIZERS

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Fig. 4

Solubility  $C^*$  (for  $\Delta C = 0.1 \text{ mol/l}$ )

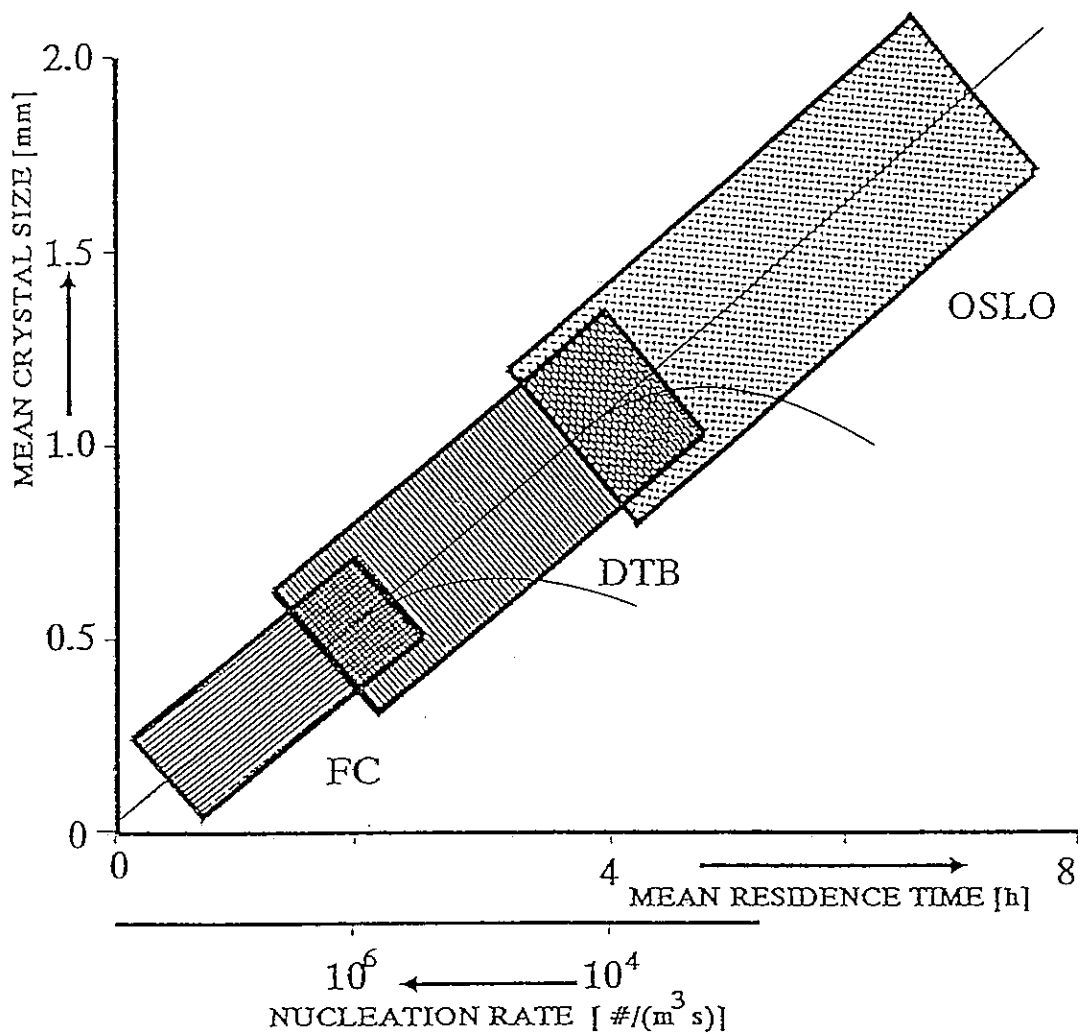


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MEAN CRYSTAL SIZE VERSUS  
SUPERSATURATION

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Fig. 5

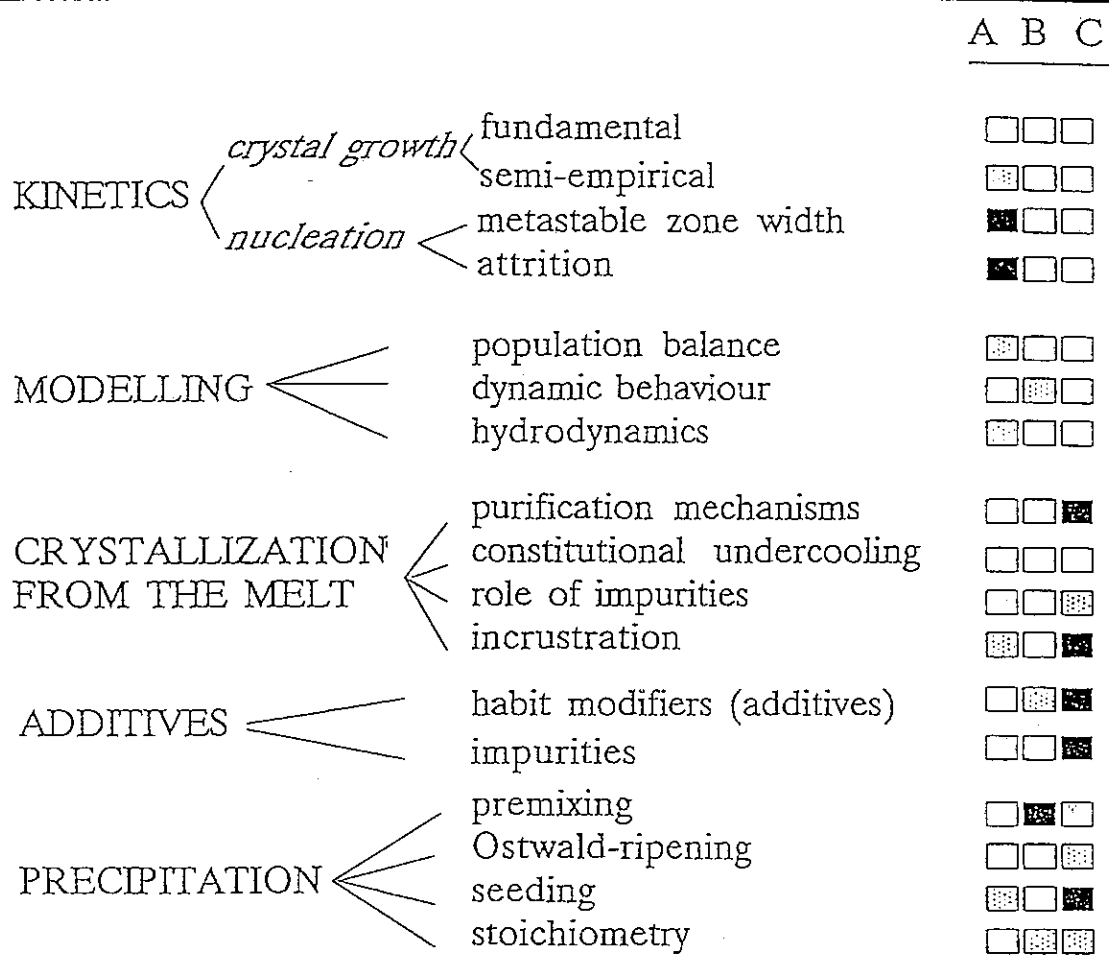


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CRYSTAL SIZE AS FUNCTION OF  
RESIDENCE TIME AND NUCLEATION RATE

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Fig. 6



A: Crystallizer layout  
 B: Operation  
 C: Process development

No relevance  
 Applicable to some extent  
 Very usefull


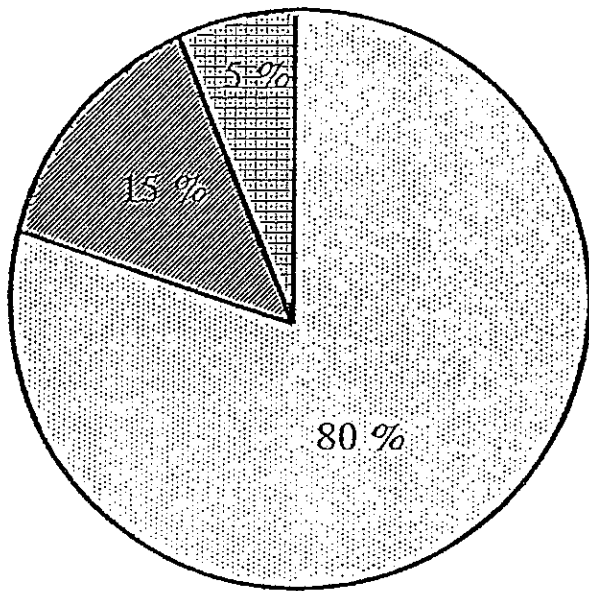
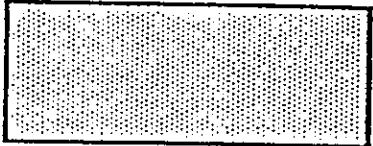
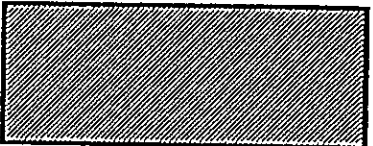
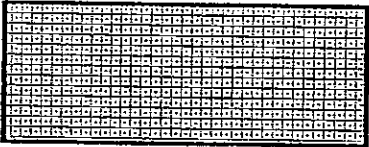
<b>MANNESMANN ANLAGENBAU</b>	<b>PRACTICAL USES OF RESEARCH IN SEVERAL AREAS</b>	
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Fig. 7



80 %  
  
*No specific requirements*

15 %  
  
*Specific requirements  
 (covered by experience)*

5 %  
  
*Specific requirements  
 (fundamental work  
 necessary.)*

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REQUIREMENTS ON  
 CRYSTAL SIZE DISTRIBUTION

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Fig. 8