# SITUATION OF PLANT CONSTRUCTION IN INDUSTRIAL CRYSTALLIZATION – A PROCESS INTENSIFICATION

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This contribution shall demonstrate the changes in the field of Industrial Crystallization since the first symposium during the sixties concerning the demands from the market and the respective responses from the specialized plant constructors. It summarizes the changes of Industrial Crystallization in the world market, the typical products from crystallization plants and the typical tasks of a plant constructor active globally in the field of Industrial Crystallization. There appears to be a growing distance between the present focus within the ISIC and the real-life situation of a plant constructor. As a result, a discussion of the present situation and the ongoing process intensification activities is desirable.

Nowadays, the market for Industrial Crystallization is focused more on combinations of separation technologies than on simple applications of crystallization. In order to analyse these changes in more detail, the Messo installation references were evaluated on the basis of distribution by region, by product and by complexity. The results show an intense and continuing movement of the market away from simple recurrent applications. There is an increasing demand for combined processes and process intensification. Typical examples are processes involving fermentation broth and waste water treatment, while activity in classical markets for such plants as for Sodium sulphate, salt or potash is less important. This new demand has been forcing plant constructors to strengthen interdisciplinary cooperation and to form teams trained in creative process design and process intensification. It would be of significant value to the ISIC to lead the development of new processes stemming from our core technology of crystallization.

## 1. Introduction (where we are)

*Process Intensification* is defined as: *"Analysis and consideration of technical and also economical requirements by the use of innovative methods during the development of new technologies and their optimization"* [GRE98].

This seems to be valid not only for the design and optimization of industrial processes but also for institutions of communication like the International Symposium on Industrial Crystallization. Whereas the early symposia had focused on such topics as plant design and plant operation for Industrial Crystallization, interest in these areas has been weakening since the nineties. A flashback shall help to recall some of the details *(please note that the selection of the papers quoted is following author's point of view and might not be representative from other positions)*.

In 1967 Synowiec [SYN67] presented a paper in which he described the potential of improving average crystal size in batch crystallization under controlled or natural cooling, at various residence times. In the same year Matusewitsch and Baranov [MAT67] noted the negative influence of increased residence time at higher energy input levels in a FC crystallizer on the average crystal size. These findings were immediately applied in the field. In 1975, during the first ISIC under the sponsorship of EFCE, Wöhlk and Hofmann [WÖH75] reported on a new vacuum cooling crystallization plant for potash from Sylvinite, which had been set up one year before, in Mulhouse, France. The plant had a production capacity of some 140 t/hr KCl made in 14 modern Turbulence crystallizers of 6 m diameter designed to produce crystals of granular, fertilizer grade quality.

One symposium later, in 1978 it was Larson [LAR78], who explained the influence of fines dissolving and classification (Fig. 1) on the breadth of a crystal size distribution from a DTB crystallizer, and in 1981 Wöhlk [WÖH81] described how to improve the operation cycle of Oslo crystallizers from 3 to 30 days by rearranging the internal flows.

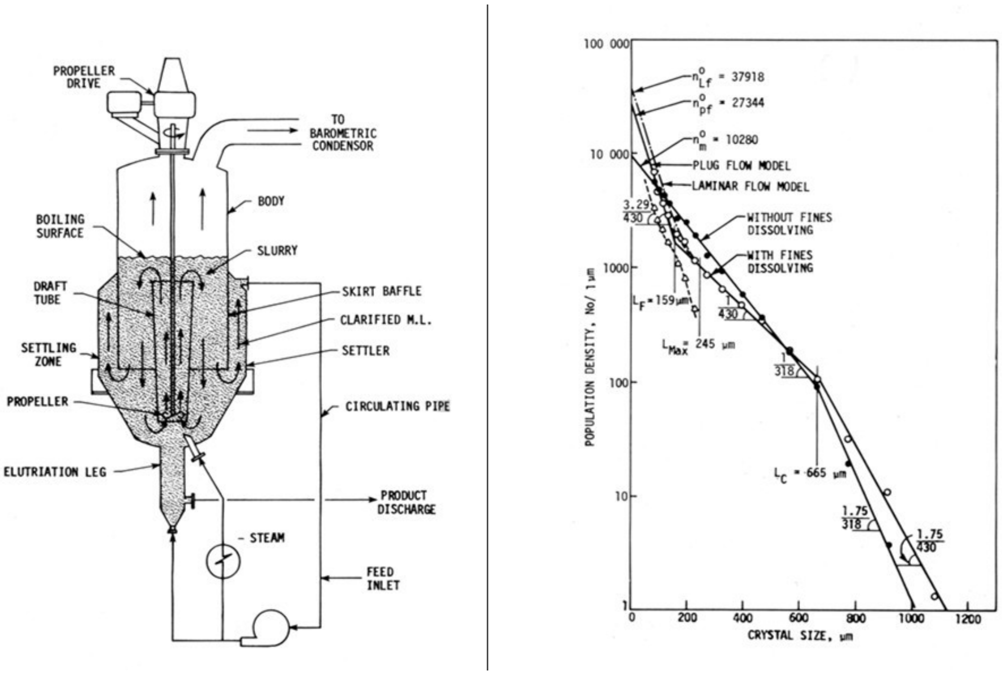


Fig. 1: Population Balance showing the Fines Destruction and Classification in a DTB Crystallizer [LAR78]

De Jong [DEJ84] and Mersmann [MER87] in 1984 and 1987, respectively, summarized the need to describe in detail the influence on the product CSD of the kinetics and related processes in actual crystallizer units, and the achievements in these endeavours to that point. Interest in these areas begun to lessen in 1990, when the paper of de Jong et al [WÖH90] proposed that any further investment in the development of crystallizer design would have to be balanced carefully against the potential savings. One of the authors' arguments was that there already existed a sufficient number of tools to solve more than 80% of the task requests safely without intense R&D studies. They defined only 5% of the task requests to be subject to fundamental studies. The remaining needs for fundamental studies were defined to be process simulation tools, habit modification and a screening method for those impurities, which may cause crystal shape problems. Crystallizer Design had matured.

In the symposia that followed, the focus of contributions moved away from the design of crystallizers for bulk crystallization from solutions. The new, hot topics were, among others, melt crystallization, habit modification and the batch operated crystallization of pharmaceuticals, and procedures to produce a specific polymorph.

If what was thought in 1990 were to be revisited today, one would say that it had not been strong enough. Evaluating the list of Messo references since 1960, the result is: the market demand for a certain, well defined crystal size distribution seems to be generally overestimated: 92% of all crystallizers built in this period were simple FC-type crystallizers, the Turbulence (DTB) reached about 7% and the fluidized-bed crystallizer (Oslo) came only to 1% (Fig. 2 left). The large number of FC crystallizer installations demonstrates that the market has obviously not been very demanding of large crystals with specific size distribution.

In examining the number of task requests without specific requirements as compared to those with special needs, the figures of de Jong et al from 1990 [WÖH90] are confirmed. Today, that number is closer to +90% rather than +80% (Fig. 2 right). There has always been more interest lengthening operation cycles, on reducing energy consumption, on incrustation-free operation, trouble-free control schemes and on the right choice of construction material, rather than on obtaining a given particle size.

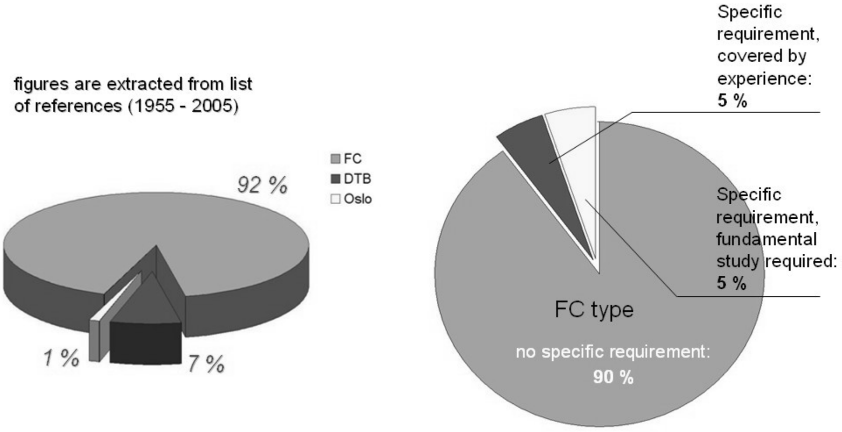


Fig. 2: Relative Frequency of Crystallizers and Importance of CSD

From the scale-up experienced plant constructor’s point of view, the existing tools for the design of crystallizers and crystallization processes can be safely described as good enough.

## 2. How do we design today

The quality targets for simple bulk crystallization from solutions to be met by crystallization are simple requirements for: crystal size, crystal size distribution, crystal shape, and crystal purity.

Crystal size: apart from any market requirements, crystal size has important process relevance. Centrifugation of the suspension delivers a much dryer filter cake than filtration. There is far less adherent mother liquor on the product crystals in the case of centrifugation, and purity requirements are easier to meet. In order that centrifugation is used, instead of filtration, the average crystal size should be least around 0.2 mm. There are available three basic types of crystallizers to cover crystal size requirements. The FC-type is selected if smaller crystal sizes are acceptable, while the DTB and the fluidized-bed crystallizer are used to produce the larger particles. Some adjustments to the particle size obtained can be made by varying energy input and the utilization of/or variation of fines dissolving capacity:

CSD: Special demands for the uniformity of a distribution can be fulfilled by classified removal.

Crystal shape: The successful modification of a crystal shape, e.g. by applying tailor-made additives, remains out of everyday reach due to the complexity and time requirements of test work The tools available to the plant constructor are only attrition or the use of some already known additive, if certain habit modifications are required.

Crystal purity: If the average crystal size is larger than 0.2 mm, if the size distribution is close to the normal MSMPR uniformity number of $n_{RRSB}=2.3$ (C.V.=50) and if the crystal shape is not an extreme needle or plate, purity can be said to depend only on size of investment.

The minimum average crystal size of 0.2 mm can be achieved by avoiding spontaneous nucleation during the steady state operation. Exceptions are estimated to be less than 5% of industrial applications. The avoidance of spontaneous nucleation in steady state operation of industrial crystallizers is one of the most important targets in the design of a crystallizer. This target is reached by fixing a certain $\Delta C$ ratio (production rate/recirculation rate), which must keep the tip supersaturation in the crystallizer safely below the metastable range of supersaturation; the desupersaturation rate, the crystal growth rate must also be considered in this facet of the design. The metastable range and the desupersaturation rate (as function of suspension density), must be defined during the process development. The method of how the tip supersaturation might be limited by setting the max. $\Delta C$ ratio is illustrated in Fig. 3. This figure shows an FC-type crystallizer with indication numbers in several positions, which are also plotted in the solubility diagram shown. The dotted line is the borderline of the metastable range. This example is for a vacuum cooling crystallizer, but the principle is valid for most crystallization processes

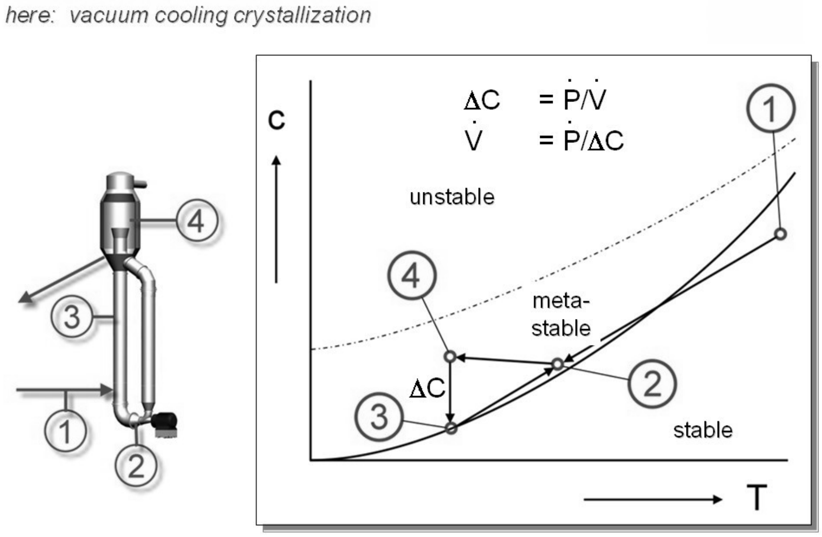


Fig. 3: Supersaturation Control in Continuous Crystallizers

In the vacuum cooling process the feed solution (point 1) must be hotter and more concentrated than the saturated mother liquor inside the crystallizer (point 3). Both liquors are mixed at the feed point. The resulting mixture (point 2) can already show a supersaturated concentration, which if created, must be kept within the metastable range by shifting the feed point or by selecting more than one crystallization stage. The solution (suspension) is recirculated through the crystallizer. The solution starts boiling when passing the liquor level. This boiling is forced by adiabatic expansion of the solution, which is superheated in regard to the controlled vapour conditions. By the evaporation of solvent the solution is re-cooled to mother liquor temperature and forms a supersaturation (point 4) which is dependent on the solvent loss and the cooling. This tip supersaturation must be kept within the metastable range, preferably in the middle of the metastable supersaturation range. When assuming the supersaturation in point 3 to be negligible under any condition, an increase of the recirculation rate will decrease the tip supersaturation (point 4) to lower values and vice versa. This is the common principle used to avoid spontaneous nucleation under steady state conditions. The respective recirculation rate is already selected during the design.

This principle is applied to all basic types of crystallizers (Fig. 4), the FC, the DTB and the Oslo type and was so long before a theory of crystallization was established. The figure below shows units arranged as evaporative crystallizers, i.e. with a calandria heater. In all of these crystallizers the recirculation rate to control the tip supersaturation should be similar for similar production rates of a certain substance. These recirculation rates are always big enough to keep the product crystals suspended in the crystallizer column and obtain high heat transfer rates.

In the FC-type the heater is placed inside the recirculation line, requiring an elbow impeller pump to maintain the recirculation rate and overcome the pressure loss of the system (mostly due to the heater), which is around 2 m l.c. The tip speeds of these pumps reach to 20 $ms^{-1}$, which can increase the energy involved in the impact between crystal and impeller. The result of the relatively high energy input and the consequently high secondary nucleation rate is a moderate average crystal size of up to 0.6 mm. The residence time typically varies between 0.5 - 2 hours. Longer residence times would be counterproductive. Nevertheless, the FC-type is the most common crystallizer worldwide.

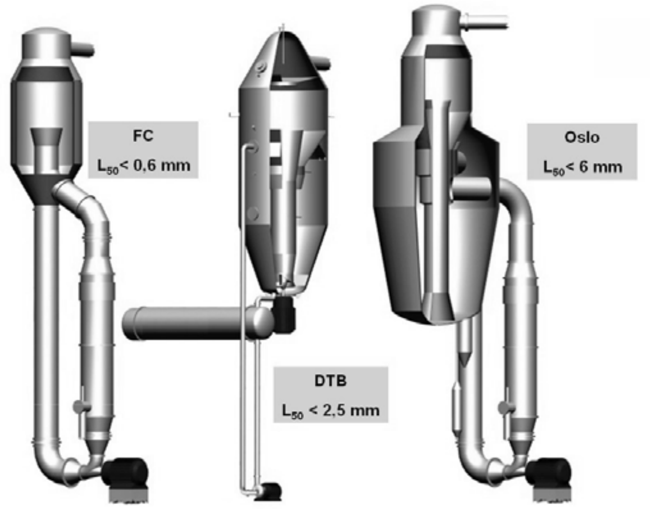


Fig. 4: Basic Types of Continuous Crystallizers

The Turbulence (DTB) crystallizer design is characterized by a significant reduction in energy input. Consequently, the secondary nucleation rate is lower and the average crystal size becomes bigger. The crystal size is further increased by means of an additional, external recirculation circuit for the heater. The external loop is operated with clarified liquor so that nucleation cannot occur. The recirculation rate is sized on the basis of a $\Delta T$ across the heater which in these cases may vary between 5K and 15K.

The internal recirculation, which controls the tip supersaturation, is driven by a large stirrer or a bottom-mounted impeller pump. Compared to the FC crystallizer the pressure drop in this internal circuit is substantially lower. This lowers the energy input accordingly and thus the secondary nucleation rate is reduced proportionally. Due to the much lower pressure loss in the internal recirculation, a much lower impeller tip speed can be used (as compared to the FC impeller pump with its 20 $ms^{-1}$). The impact between crystals and blades are not as intense and breakage of crystals is reduced. Both of these features contribute to the much bigger average crystal size (< 2.5 mm) obtained in a DTB. However, the greatest contribution to producing large crystals is the fines dissolving, which occurs in the external heater circuit. The clarification of the recirculated liquor in the internal baffle zone leaves most of the crystalline mass inside the crystallizer, but a large number of smaller particles are carried over by the recycle stream and enter the external circuit. These are redissolved when passing through, or after leaving the heater. This feature, however leads to cycling of the average product size in DTB crystallizers. If cycling of the CSD is unacceptable, seeding the crystallizer, with particles larger than a critical crystal size, can help control the size fluctuations. Due to the reduced nucleation rate, the residence time can be higher than in FC-type crystallizers and typically varies between 1.5 and 4 hours. Longer residence times become, again, counterproductive. DTB crystallizers are sometimes equipped with an elutriation leg to withdraw a classified suspension. This improves purity and uniformity of the product.

The Oslo-type is the crystallizer with the largest volume. If operated as real fluidized-bed crystallizer (completely clear overflow), the residence time is often longer than 10 hours. This does make sense only in those crystallizers which show a nucleation rate approaching zero. All the crystals are kept in a fluidized bed within the suspension chamber. The recirculation pump (elbow-type) is only operated with clear liquor (ideal case) which overflows from the suspension chamber. Any fines in the clear liquor are re-dissolved in passing through the heater. As a consequence of this intense fines dissolving, the average crystal size in the fluidized bed can become extremely large, e.g. even 5 - 10 mm. A second consequence is an even stronger cycling behaviour than that of DTB crystallizers. All Oslo types must be seeded to avoid that cycling. Oslo crystallizers are usually operated with “salt legs” for the withdrawal of crystals to improve the uniformity of the product.

While modern plants use crystallization as a routine unit operation, usually it is not the crystallizer to which most of the development work is focused, but to peripheral issues upstream or downstream.

For example, in the classic pickling bath regeneration, what people have been working on is not the crystallizer itself, but the automation and energy usage, details on construction like a suspended impeller pump, and the selection of sulphuric acid resistant materials of construction for equipment and buildings.

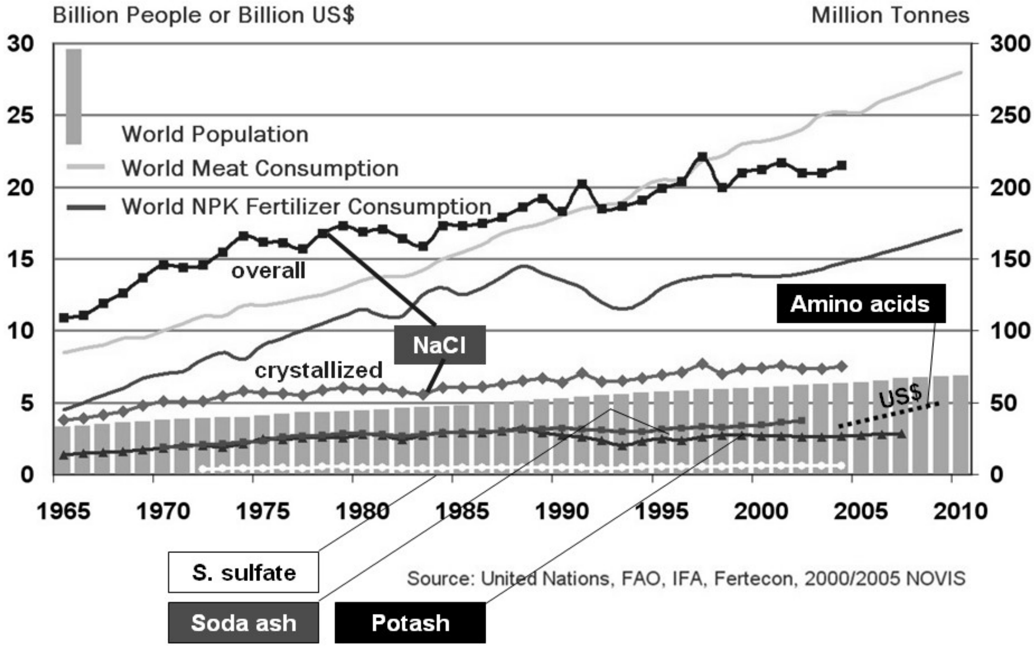
Similarly, in the crystallization of Sodium sulphate from chromium chemicals recovery, it is again not the crystallizer attracting process development attention, but the complete removal of the hexavalent Chromium upstream the crystallization process. Without this upstream treatment the sodium sulphate product from the FC-type crystallizer cannot fulfil international quality standards.

## 3. What does the future hold?

Just as the design of crystallizers became routine, the market for plant construction began to shift with emphasis on the demand for more complex combinations of the crystallization unit operation with complementary technologies. The classical crystallization market lost importance.

It is difficult to make predictions regarding the market for crystallization plants. The number of available projects is strongly dependent on the economy of the country in which the plant is and the world demand for the product. The need for some crystalline products disappears while markets for new products arise continuously. Demand is difficult to predict. Moreover, crystallization processes are distributed over the entire chemical, life science, pharmaceutical, food, and even the steel industry, worldwide. Market changes and developments require the immediate re-orientation of the plant constructor. This reorientation is needed not only for every developing project, but more so with respect to the plant constructor's technology and development capability, i.e. its personnel profile.

In preparing a forecast of market chances and product changes, it is helpful to look at the world population increase and some of the directly or indirectly connected supply industries. Reports and predictions on the world population [TOT05] and the related demand for fertilizers and meat (market for food additives) [AGR04] reflect an unsteadily increasing need for NPK fertilizer, and a high demand in meat production (Fig. 5).



Source: United Nations, FAO, IFA, Fertecon, 2000/2005 NOVIS

Fig. 5: Consumption of Fertilizer and Meat vs World Population ([TOT05], [AGR04], [PAR05])

The relationship of the crystallization market to world population becomes clearer if the term meat is defined as consumption of essential amino acids like L-Lysine HCl or MSG (new products: food additives) [PAR05].

Obviously, there are products which follow the world population, while others do not: some growing faster (NPK, Amino acids) and others surprisingly slower. The world market in crystallized salt [KOS04a] is obviously proportional to the population development, whereas other mainstay crystalline products like potash (despite of being a fertilizer), sodium sulphate and soda ash from Trona behave worse ([KOS03], [KOS04b], [BUC05]).

What does this development mean for the plant construction market? How many plants will be built per year? Can that number satisfy the plant constructors in the market? Most of the inorganic chemicals in the classical crystallization market are compounds of only some elements of the Periodic Table (organics have contributed in average only about 20%). These are the Chlorides, Sulphates, Nitrates and Carbonates of Sodium, Potassium, Magnesium and Calcium. Major products among these are Sodium chloride, Sodium sulphate, Sodium carbonate and Potassium chloride. By collecting the world consumption figures of important crystalline products and the respective forecasts one can get rough estimates on the average number of plants per product to be built per year. That may be applicable for well defined products, but unfortunately difficult for the ZLD waste water market, due to that market's quite complex structure. Published growth figures are reporting a strong increase in the water reuse market, from US$2.5 billion in 2005 to US$7.8 billion in 2015 [GWI05].

On the other hand, the rise in demand for salt crystallization plants during the last decade has been, in average, 460 thousand tonnes annually. That corresponds to only one or two salt crystallization plant for rock salt mining and perhaps for one or two plants based on solar salt per year - plus the replacement of the old existing units in about the same order of magnitude. Similarly, the increase in demand for Sodium sulphate during the last decade has been 45 thousand tonnes annually. That corresponds to only one or two new plants per year. For Potash the situation is surprisingly worse. The production increase during the last decade was nearly zero and, excluding some home-made units, no new plants were built.

This shrinking market volume of mainstay products has to be shared by more than 20 internationally established plant constructors, while locally there are even more (especially in China). It is easy to understand then, that this situation is continuously challenging the search for new applications of Industrial Crystallization.

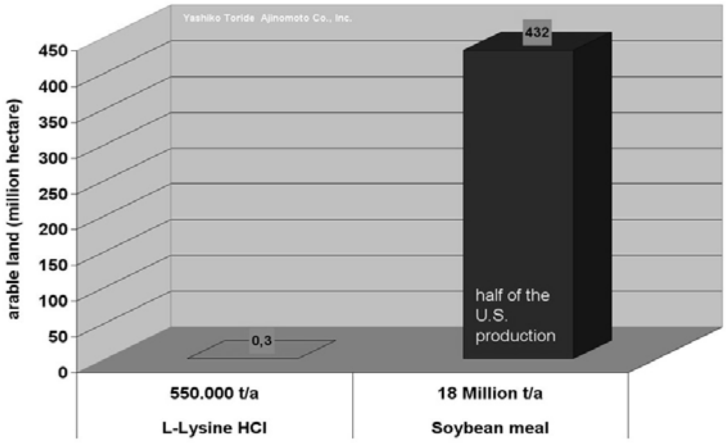
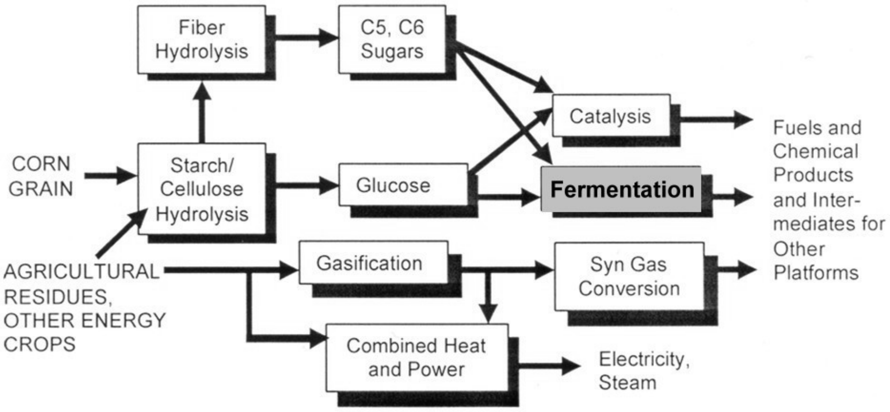


Fig. 6: Efficient Utilization of Cultivated Areas by adding Amino Acids to Animal Feed [TOR02]

One of the faster growing new product groups is obviously that of food additives, most of them produced by fermentation processes. Amino acids improve the efficiency of animal protein production and contribute to increasing protein demand (Fig. 5). The worldwide estimated usage of L-Lysine HCl, 550 000 tonnes/year, corresponds to savings of 18 million tonnes of soybean meal (and 432 million hectares of arable land to produce it - Fig. 6), which 18 million tonnes is equivalent to almost half of the soybean meal production of the USA. Typical food products produced by a fermentation route in addition to the essential amino acids expected to increase with the world population are vitamins or pro-vitamins like ß-carotene or ascorbic acid and its intermediates, hydroxy carbonic acids and dicarbonic acids. Will the biorefinery from renewable resources (Fig. 7) [PAS03] become reality?



Source: Energetics, Inc. for U.S. Dep. of Energy, 2003

Fig. 7: Biorefinery [PAS03]

In order to observe or crosscheck these market shifts in more detail, the structure of Messo's references was analysed by regions, by products and by the degree of complexity. Of course, these results cannot represent the entire spectrum of possibilities. Nevertheless, they should be representative - apart from the regional distribution - considering the presence of the one or the other competitor in these new markets.
The results are (Fig. 8):

*DISTRIBUTION BY REGION (Fig. 8 part A)*

Whereas the fifties had been characterized by installations within the national borders, and the sixties and the seventies had been focusing to Europe as well as in Germany, at present

- China has become the prime third market today.

In the early years the installations had comprised mainly only crystallizers. The scope of supply broadened to battery limits in the eighties, and today there is a certain trend in China to supply only basic engineering plus some key items. This trend reflects an increased importance of the plant constructor's process design capability. On the face of these needs, plant constructors have to adjust their personnel structure accordingly.

*DISTRIBUTION BY PRODUCT (Fig. 8 part B)*

The market regarding the demand for products has been shifting with a similar strength as in the shift to new geographical regions. Whereas the early years had been dominated by the classical inorganic and organic products, including the straight fertilizer markets and the classical pickling and spin bath regeneration, the markets of today are strong in the fields of:

- Bioproducts from fermentation broths,
- ZLD waste water treatment plants with certain requirements on condensate quality and solid product consistency, which is replacing meanwhile the old regeneration market more or less entirely.

A significant part of such projects require process design studies and process intensification which are subject to the entire downstream operation, rather than the final crystallization, which is assumed to be an old, reliable tool.

*DISTRIBUTION BY COMPLEXITY (Fig. 8 part C)*

Complexity in this study is defined as the degree of specific development effort required for the individual project.

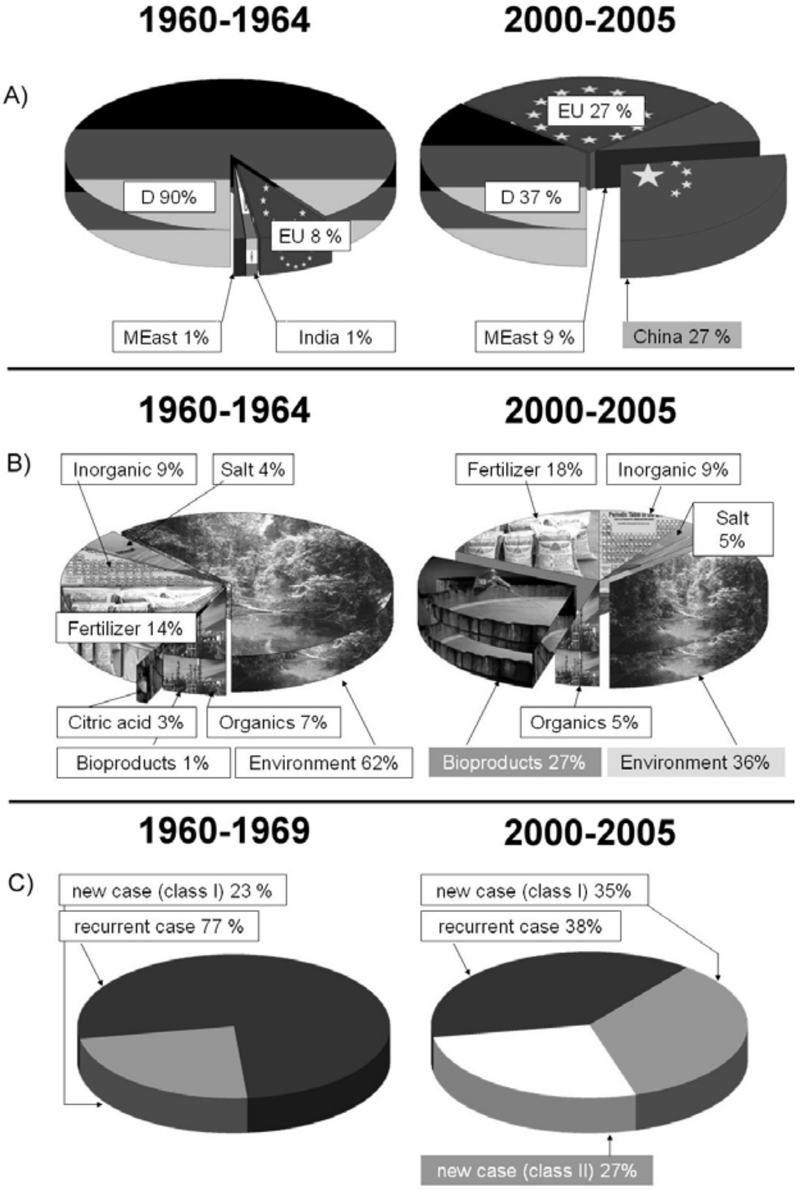


Fig. 8: Evaluation of Plant Constructor’s References (Messo)

  - additional separation steps upstream of the crystallization operation - process intensification (new case (class II))
- the classical approach, but not routine (new case (class I))
- the simple repetition (recurrent case)

These results reflect the increasing complexity of the new product classes in biotechnology and waste water treatment. Meanwhile, over two thirds of new projects require intense efforts in process design to increase process intensification. This results in two thirds of the product classes are related to either biotechnology or waste water systems.

There is agreement of the results from the Messo references with the market information reported above. The decreasing demand for classical products is offset by rising demand for downstream tasks in biotechnology to about one third of the projects. The demand for waste water (ZLD-**z**ero **l**iquid **d**ischarge) systems correlates to the large market volume expectations, replaces the former regeneration activities and makes up another third of the projects, meanwhile. The number of the original classical products is now down to the remaining third.

On first view the application of crystallization to the new market segments looks to be very easy, by doing a simple exchange of the classical synthesis or solution mining, dissolving, etc. against e.g. fermentation (Fig. 9). In the case of waste water the situation is similar, but even more complex because of the many feed sources and quality targets. The downstream technology has to recover the desired substance from a motley crowd of side products and remaining carbohydrates - the fermentation broth. A closer look reveals that things are quite different. Whereas the classical pre-treatment preceding crystallization focused on the precipitation, ion exchange or absorption (active carbon) unit operations, the fermentation broth pre-treatment is also an application for microfiltration, nanofiltration or chromatography.

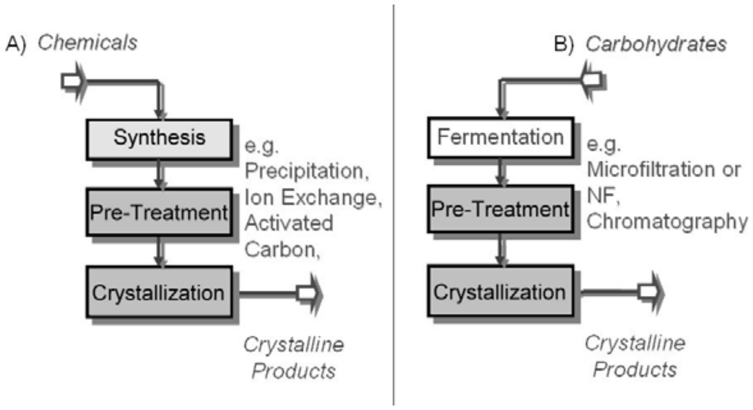


Fig. 9: Fermentation Broth Treatment Concept with Crystallization

Much more is expected from crystallization in purification, than was for the granular product of the old days. Typical applications are the crop principle (Fig. 10 top), which splits the crystallization tasks into a quality production step (first crop) and a yield responsible step (second crop), or the recrystallization principle (Fig. 10 bottom).

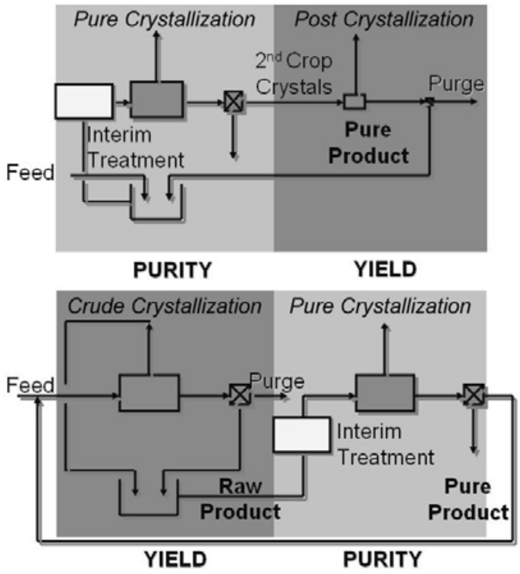


Fig. 10: Crop System and Recrystallization applied for Downstream of Fermentation Broths

Although the crop system does not have the same separation potential as the recrystallization principle, it is preferred because of its lower energy consumption. Both process principles can be equipped with intermediate treatments, e. g. an active carbon treatment preceding the stage responsible for crystal quality.

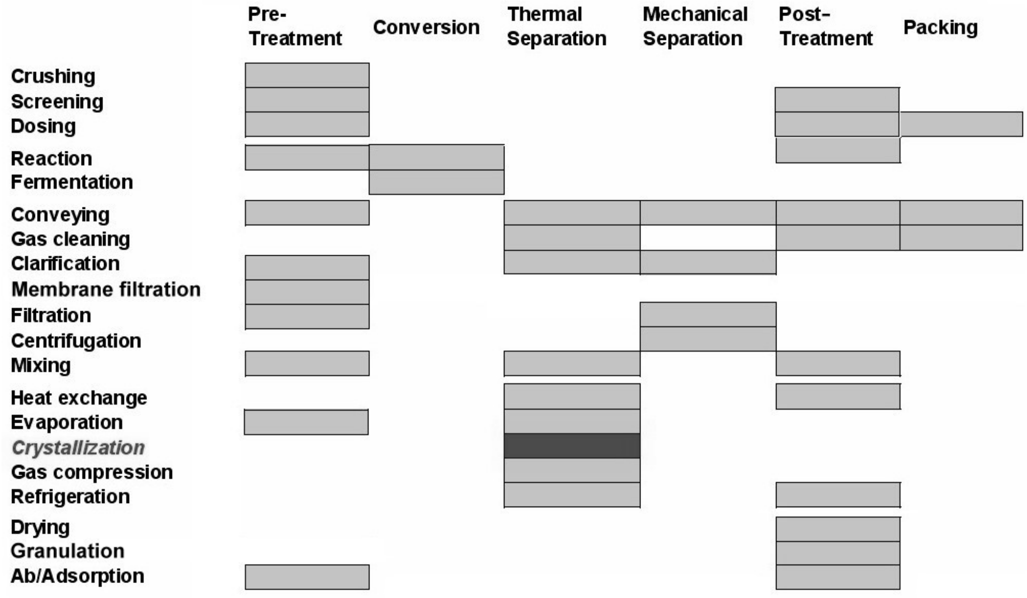
The second lively product group, the complex ZLD waste water market requires even stronger interdisciplinary cooperation in technical and economic matters. This is so because time schedule and costs are always shifting the pressure on the development of the related process design. Often, crystallization becomes only the solidification step at the tail of a downstream process. In arid areas, e. g., the recovery of pure water from dilute aqueous waste, free of contamination by various organics and inorganic compounds can be much more important than the final crystallization step. Nevertheless, even then the final crystallization has to be designed and operated as a crystallization system, which needs to run over long periods without problems caused by incrustations, unexpected boiling point elevations, high viscosities, etc. In other occasions it might be helpful to recover one of the major solutes from process waste water in a certain, marketable quality to improve the cost situation and to thus refinance the waste water activity. In this example, of course, the crystallization step plays the dominant role.

## 4. Consequences

The major unit operations composing an Industrial Crystallization plant are listed in Fig. 11 and listed in order to the upstream or downstream position of the operation with respect to the basic crystallization. In order to serve the needs of downstream processes in a satisfactory manner, the need for interdisciplinary cooperation unit operation specialists becomes evident.

Applied Industrial Crystallization must be regarded as a mature unit operation which is not applied only to the design of crystallizers or simple crystallization factories anymore. The demand for the design of entire processes surrounding the core operation of crystallization has become typical. The fulfilment of this demand is an attractive and growing market. Unlike the developments in the design of crystallizers from the seventies to the nineties, this new market need seems to not be sufficiently represented within or recognized by the ISIC.

To remain on the cutting edge in the evolution of Industrial Crystallization, it would be essential for ISIC to be the major forum for those new processes around the core of the crystallization unit operation.



| | Pre-Treatment | Conversion | Thermal Separation | Mechanical Separation | Post-Treatment | Packing |
|---|---|---|---|---|---|---|
| **Crushing** | ▨ | | | | | |
| **Screening** | ▨ | | | | ▨ | |
| **Dosing** | ▨ | | | | ▨ | ▨ |
| **Reaction** | ▨ | ▨ | | | ▨ | |
| **Fermentation** | | ▨ | | | | |
| **Conveying** | ▨ | | ▨ | ▨ | ▨ | ▨ |
| **Gas cleaning** | | | ▨ | | ▨ | ▨ |
| **Clarification** | ▨ | | ▨ | ▨ | | |
| **Membrane filtration** | ▨ | | | | | |
| **Filtration** | ▨ | | | ▨ | | |
| **Centrifugation** | | | | ▨ | | |
| **Mixing** | ▨ | | ▨ | | ▨ | |
| **Heat exchange** | | | ▨ | | ▨ | |
| **Evaporation** | ▨ | | ▨ | | | |
| ***Crystallization*** | | | ■ | | | |
| **Gas compression** | | | ▨ | | | |
| **Refrigeration** | | | ▨ | | ▨ | |
| **Drying** | | | | | ▨ | |
| **Granulation** | | | | | ▨ | |
| **Ab/Adsorption** | ▨ | | | | ▨ | |

Fig. 11: Unit Operations applied in Downstream Processes with Crystallization

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