

# Crystallization

**Range of Products**

**Individual plants for the chemical, pharmaceutical and food processing industries**

(Unit operation, evaporation, crystallization, thermocompression)

- Crystallization plants
- Evaporation plants (all concentration under significant scaling conditions)

**Crystallization and evaporation technologies for the chemical, pharmaceutical and food processing industries, e.g.:**

(Entire technology concepts, based on precipitation, evaporation, crystallization)

- Common salt production plants
- Reaction crystallization plants for several base/acid reactions

**Plants for environmental protection**

(Based on precipitation, evaporation, crystallization)

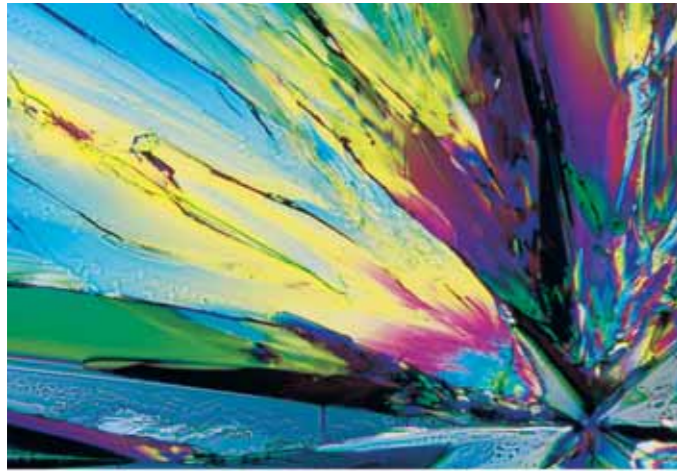
- Pickling bath liquor recycling plants
- Landfill leachates concentration plants
- Industrial waste water ZLD plants
- Treatment plants for slags from the secondary aluminum industries

# Crystallization

In Theory and Practice



*... we know how*



Crystals of citric acid  
in polarized light

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## Messo, synonym for crystallization



MESSO's contributions to the field of crystallization began about fifty years ago, originally under the name Standard-MESSO Duisburg; since that time, MESSO has been a crucial participant in crystallization and related purification technologies, throughout the world. MESSO's broad and very successful involvement in the chemical, food, steel, and environmental industries is proof of the acceptance it has gained within the international chemical engineering community. At the turn of the century, MESSO boasts of over thousand installations and references of its abilities in the design, construction, start-up, de-bottlenecking, and turnkey delivery of evaporation and crystallization systems.

MESSO's expertise encompasses all basic types of crystallizers for the crystallization from solutions, such as the forced circulation or draft-tube (MSMPR) crystallizer, the turbulence (DTB) crystallizer, and the fluidized-bed (OSLO) crystallizer. MESSO is thus in a unique position to address the special needs of each of its clients, depending on the required product crystal quality and size.

In addition to the centerpiece of a crystallization system, the crystallizer, MESSO offers its clients the supply of optimized peripheral equipment, in several levels of involvement. MESSO routinely supplies upstream and downstream components, such as the preconcentration (in multiple effect, mechanical vapour recompression, flash, and other evaporator configurations), the dewatering (thickening, filtration or centrifugation), drying, solids handling and packaging. MESSO also supplies piping and

instrumentation and process control systems for its plants, installations in pre-fabricated and modularized sections, and turnkey installations, as required by the client.

MESSO is a leader in its field through in-depth reviews of its operating installations and research and development. The Research and Development Department of MESSO is housed in a two-hundred-square-meter facility, equipped with test units that simulate batch and continuous operation of all basic types and configurations of crystallizers. It has in-house analytical capabilities for direct determination of concentration, supersaturation, and other physical properties of the subject process liquors. Not only the design of crystallizers but the development of optimized separation processes for our clients' needs is in the focus of MESSO chemists and engineers.

In order that its know-how is continually enriched with cutting-edge developments in the field of crystallization, MESSO has established the close cooperation of several leading European Universities' Research Centers for information exchange.

MESSO engineers share their wealth of practical experience with the international chemical engineering community through presentations during scientific symposia, publications of pertinent articles and the arrangement of national and international crystallization seminars. MESSO contributions have been included in several technical handbooks and the well-known Ullmanns' Technical Encyclopedia.

This state of experience, broad technical background, updated skills and in-depth research are brought to bear on each and every project MESSO handles. The results are tailor-made solutions that combine optimal investment with plant functionality, reliability, modern technology, safety, and respect for the environment. MESSO engineers always look for the most feasible plant configuration which – at the end – is also the cheapest investment.

A large part of MESSO's business comes from repeat clients; this is the best testimony for the quality of our work, the commitment of our engineers, and the performance of our equipment.

*... we know how*



## Crystallization in history and presence



the birth of crystallization technology, that aimed at improving the methods and equipment used in crystallization operations. Modern crystallizers can boast specific production rates that are several orders of magnitude higher than solar ponds, have low manpower requirements, and low production costs.

The specific requirements of a crystallizer can vary widely, depending on the nature of the product, and its intended use: pharmaceutical and food products require higher purity, for example, while fertilizers need larger crystal size; the crystal size and final moisture are not as important in crystallization systems which produce an intermediate compound. There are cases where the real product of the crystallizer is the solvent: crystallization is used to separate from the solvent the compounds that make it impure. Further, there are cases where crystallization is used to concentrate a solution, by crystallizing and removing the solvent (freeze concentration).

One quality that is present in all crystallization systems, regardless of the final use of the solvent or the crystal, is the ability to separate the crystals from the mother liquor. This ability is a function of the crystal size, and, by extension, a function of the separation equipment that can be used. Centrifugation is by far the most efficient separation method, if the average crystal size is large enough. It is therefore

In antiquity, settlements developed around, and exploited sites where salt was easily available, whether as rock, brine, or derived from solar evaporation. For example, salt was produced in the Pharaonic Egypt at the Nile Delta; similarly, the Romans recovered salt at Ostia seacoast (near Rome) and the same happened all over the world (e.g. in China). These and many other production sites prove that crystallization from solution is one of the oldest unit operations practiced by humankind.

While crystallization in solar ponds is still in regions with plentiful sunshine, its low production rate and mediocre product purity prevents this technology to be used generally. As the world developed through industrial age, the demand for crystalline chemicals increased in variety, quantity, and quality. This led to

logical to expect that of the characteristics of a crystallizer, the crystal size it produces is of great importance.

The possible crystal size of a given compound is dependent on its chemical and physical properties, and those of the solution in which it is dissolved. In parallel, the crystal size is

the attrition, and the growth rate of crystals, and by destroying a fraction of the smaller crystals present in the crystallizer itself. Inattention of these parameters, on the other hand, can contribute to a degradation of the crystal size.



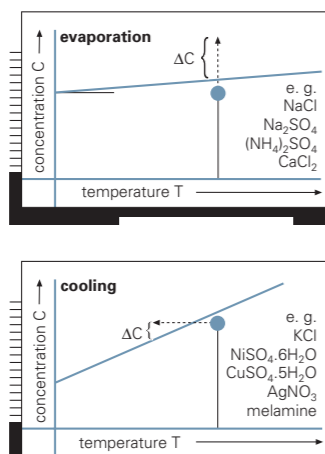
A 16th century salt works

dependent on the equipment used to crystallize it, and the method by which the equipment is operated.

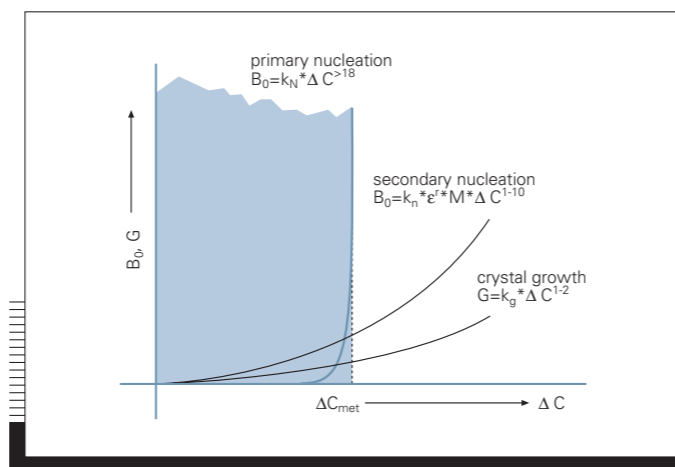
The crystallizer used can contribute to improving the crystal size, within physical and energy boundaries, by controlling the nucleation,

## Crystallization in theory and practice

A key parameter for crystallization is the supersaturation. Supersaturation is the temporary increase of concentration of the solute in the solvent above its equilibrium, and is produced by evaporation, cooling, chemical reaction, salting out, etc. The area over the normal solubility, in which a system can be supersaturated, is also called the "metastable" region. Supersaturation is the driving force of crystallization. Proper control of supersaturation is of critical importance in achieving acceptable results.



1. Crystallization processes, shown in equilibrium (solubility) diagrams



2. Kinetics of crystallization

The most common crystallization operations today are those of evaporative crystallization and of indirect and direct (vacuum) cooling: In the former, crystallization occurs after some amount of solvent is removed, and this is due to the relatively "flat" solubility of the system at hand (Fig. 1a). In the latter case, the solubility is rather steep (Fig. 1b), and supersaturation can be achieved by cooling easily.

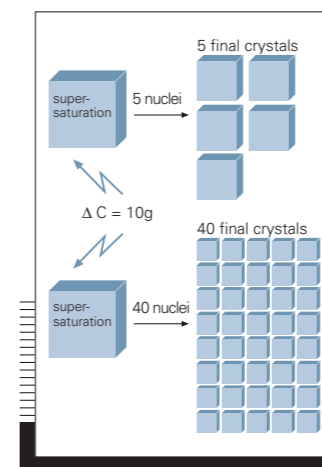
The crystal growth rate, a parameter that measures how fast a crystal grows, is, for most systems, exponentially dependent on the supersaturation (Fig. 2). However, the end result of the crystal size obtained in a crystallizer is not a matter only of the growth rate, but also of the nucleation rate (how many crystals take part in crystal growth), and the attrition rate (how easily crystals break, and how small are the broken fragments). The nucleation rate is also a function of the

supersaturation, and is affected by supersaturation to a far greater degree than the growth rate (Fig. 2). As a result of these very complex relationships, the supersaturation at which a crystallizer will operate must be chosen with great care.

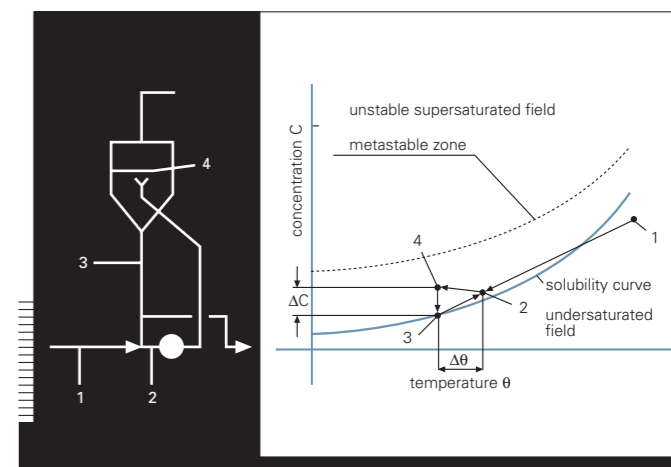
There are two common types of nucleation mechanisms. Primary (homogeneous) nucleation occurs at the onset of crystallization, when the concentration of the solvent exceeds the metastable region, and secondary nucleation, which is caused by contacts between a crystal and another surface, and occurs within the metastable region (Fig. 2). Crystal-to-crystal and crystal-to-impeller contacts are the

most common sources of secondary nucleation. Secondary nucleation is therefore affected by the mixing energy input to the crystallizer.

Combining these characteristics of crystallization, it can be said that large singular crystals are formed at low nucleation rates. Fig. 3 is a simplification (exaggerated for purposes of illustration) of this premise, and concerns two crystallizers that have the same amount of supersaturation, 10 g, from which crystals will grow. This is to demonstrate the strong influence of the nucleation rate on the mean crystal size. Due to the two different nucleation rates (5 nuclei and 40 nuclei) the result are two different crystal sizes; either 5 crystals of 2 g each or 40 crystals of 250 mg each.



3. Influence of nucleation on crystal size



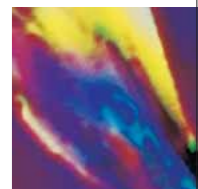
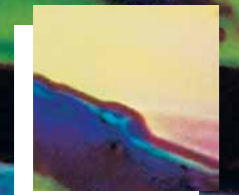
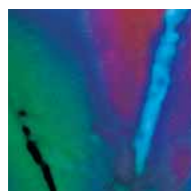
4. Control of tip supersaturation (vacuum cooling crystallization)

Most crystallizers need to produce large singular crystals, because this improves crystal purity and handling characteristics, and very often the crystalline product's marketability. To achieve a larger crystal size, it is therefore important to:

- Control the supersaturation in the crystallizer so that it does not exceed the metastable region;
- Choose an operating point of such supersaturation that growth rate is maximized;
- Optimize the mixing energy input so that supersaturation is controlled, while secondary nucleation is minimized.

As can be seen from the above, the method and intensity of mixing in a crystallizer is very critical, as it is what most influences the supersaturation and secondary nucleation of the system. Mixing, therefore, is a basic design feature in a crystallizer unit. The instan-

aneous operation cycle of a typical vacuum cooling FC crystallizer, with respect to the solubility of a system, is illustrated in Fig. 4. The fresh feed at temperature and concentration represented by point (1) enters the crystallizer and is mixed with the crystallizer contents that are at concentration and temperature (3). The resultant mixture is at point (2), passes through the boiling surface of the slurry in the crystallizer. Upon boiling, the solution reaches point (4), which is well into the metastable zone. The supersaturation generated in this way is consumed by crystal growth of crystals present in the crystallizer vessel, as the supersaturated liquid is cooled adiabatically to point (3), and the cycle is completed.



Since it is important to maintain the peak supersaturation (point 4) within the metastable zone, the location of point (2), and more importantly, that of point (4), can be adjusted, by designing the recirculation rate in the crystallizer.

If the supersaturation generated in one cycle is not completely consumed by the end of the cycle, the starting point for the next cycle will be somewhat further from the saturation curve. After some time, the whole cycle will migrate so far into or even above the metastable zone, that it will adversely affect crystal growth and nucleation. It is therefore important to provide sufficient opportunity (efficient mixing) and suitable sites (sufficient crystal surface) for the supersaturation to be consumed. Otherwise, the crystal size will suffer, and the crystallizer will be subject to incrustations.

The above ideas are embodied in the two kinetic equations below. The mass deposition rate ( $dm/dt$ ) resp. the consumed supersaturation per cycle time is dependent on the surface of suspended crystals ( $A$ ) and on the level of supersaturation ( $\Delta C$ ). Secondary nucleation  $B_0$  depends on dissipated mixing energy ( $\epsilon$ ), suspension density ( $m$ ) and level of supersaturation ( $\Delta C$ ):

$$\frac{dm}{dt} = k_g \cdot A \cdot \Delta C^m = - \frac{d(\Delta C)}{dt}$$

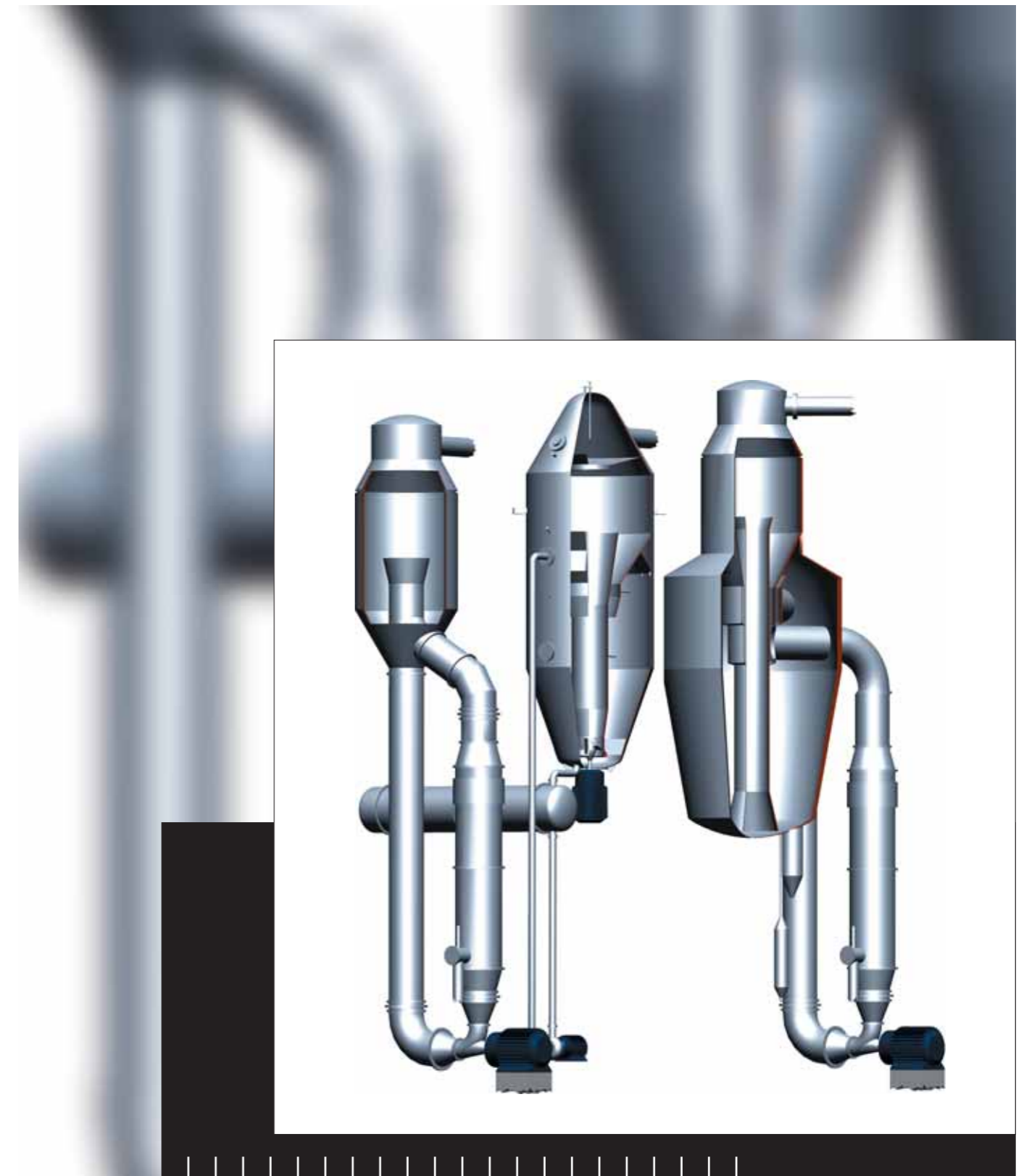
Crystal size is influenced by the time that the crystal stays in the crystallizer (retention time), where, under proper operating conditions, it may grow. There is, however, a competing quality in this arrangement, that affects the crystal size adversely. Mechanical attrition ( $G_a$ ) is the rate of removal of material from a crystal (as opposed to  $G_k$ , the linear, kinetic crystal growth rate), and it is dependent on the crystal retention time,

$$B_0 = k_N \cdot \epsilon^r \cdot m^i \cdot \Delta C^n$$

the magma density, the mixing energy and the hydrodynamic design of the system. It is therefore to be expected that under certain conditions, crystal size will peak at a certain retention time, and will thereafter become smaller, as  $G_a$  overpowers  $G_k$  and the effective crystal growth rate is minimized.

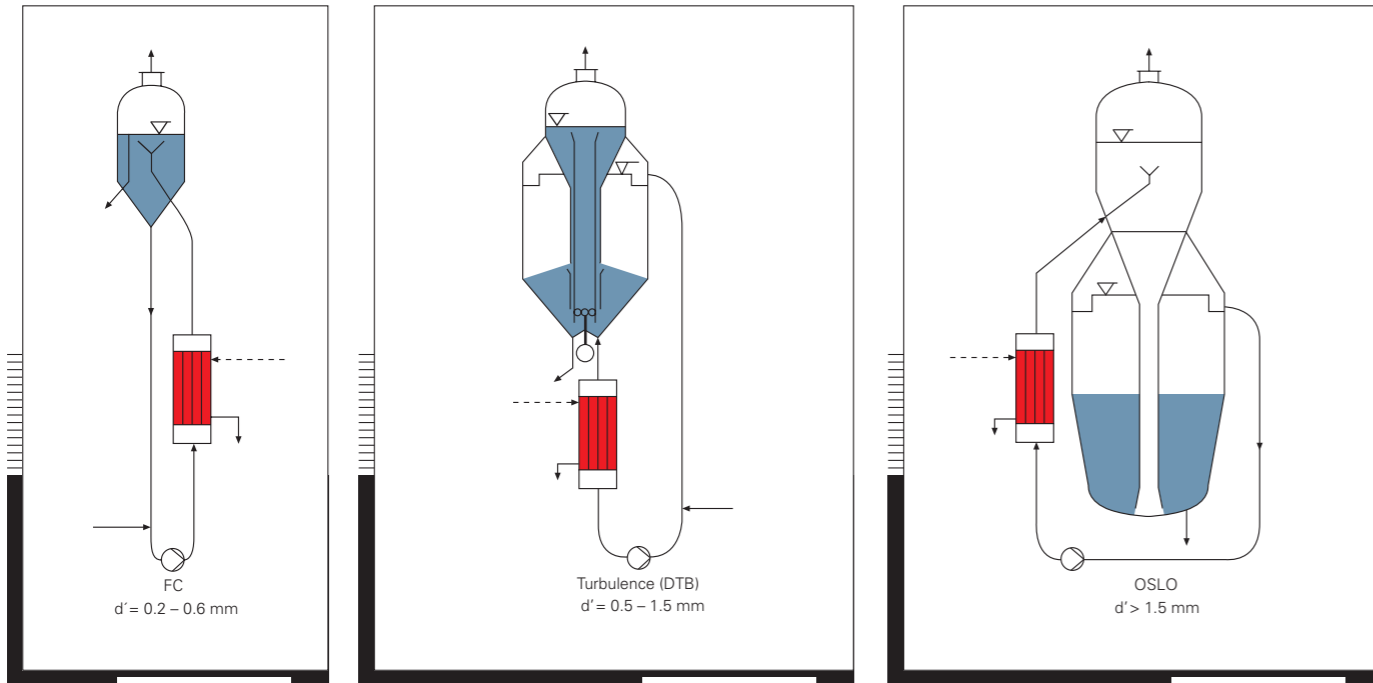


## Types of crystallizers



MESSO-type crystallizers: FC, DTB, OSLO

## Types of crystallizers



1. Forced circulation (FC) crystallizer

2. Turbulence (DTB) crystallizer

3. OSLO crystallizer

All this is considered in modern types of continuous crystallizers. Crystallizers with longer retention times are operated with less specific energy input  $\epsilon$ , resulting in lower nucleation rates. The impacts between crystals and the impeller pump blades are the most effective source for the nuclei production. These impacts are at least 100fold more effective than crystal/wall and crystal/crystal impacts. Therefore, types of crystallizers differ mainly in design and the position of the impeller pump.

### Forced circulation crystallizer

The forced circulation ("FC") crystallizer (Fig. 1) is the most common type of crystallizer in the industry. The average FC crystallizer evaporates solvent, thus increasing the supersaturation in the process liquor, and causing crystallization to occur. Most conventional FC units operate under vacuum, or at slight superatmospheric pressure.

The FC consists of four basic components: the crystallizer vessel, which provides most of the volume dictated by the residence time requirements, the circulating pump, which provides the mixing energy, the heat exchanger, which supplies energy to the crystal-

lizer (in a typical evaporative crystallization operation), and the vacuum equipment, which handles the vapours generated in the crystallizer.

Slurry from the crystallizer vessel is circulated, in plug-flow fashion, through the heat exchanger, and returned to the crystallizer vessel again, where its supersaturation is relieved by deposition of material on the crystals present in the slurry. The supersaturation is controlled so as to avoid spontaneous nucleation, by sufficient circulation capacity. The evaporated solvent is conducted to the vacuum system, where it is condensed and removed.

The FC crystallizer is used for general, simple crystallization operations, where large crystal size is not a requirement. The FC design aims to protect the crystal size from reduction from the crystallizer environment, but has no features to aggressively increase the crystal size.

### Turbulence (DTB) crystallizer

The MESSO turbulence with draft tube and baffle (DTB) crystallizer (Fig. 2) is the typical modern type of crystallizer in the industry. This crystallizer has been named so because it provides for two discharge streams, one of slurry that contains the product crystals, and another, that is mother liquor (saturated solvent) with a small amount of fines. The configuration of the crystallizer is such that it promotes crystal growth, and can generate crystals of a larger average size than could be achieved in an FC. Most conventional turbulence crystallizers operate under vacuum, or at slight superatmospheric pressure.

The turbulence (DTB) crystallizer has been studied widely in crystallization theory and can be modeled with accuracy. Its distinct zones of growth and clarified mother liquor make it

possible to define in terms of kinetic parameters, and thus growth and nucleation rates can be determined. These features make the turbulence crystallizer very suitable to mathematical description, and thus subject to good operating control.

### OSLO crystallizer

This crystallizer type (Fig. 3) originally represented the first major step in modern crystallization technology and equipment design. It was invented by F. Jeremiasen of Krystal A/S, Oslo, Finland, in 1924, and it took the name of the city in which the design originated. It is also referred to as "growth-", "fluid-bed-", and "Krystal-" type.

As the successor of Davy Powergas' and A. W. Bamforth's crystallization technology, MESSO owns all documentation of OSLO installations built by these

two companies. This background, added to MESSO's own extensive experience makes MESSO the premier designer of OSLO crystallizers in the world.

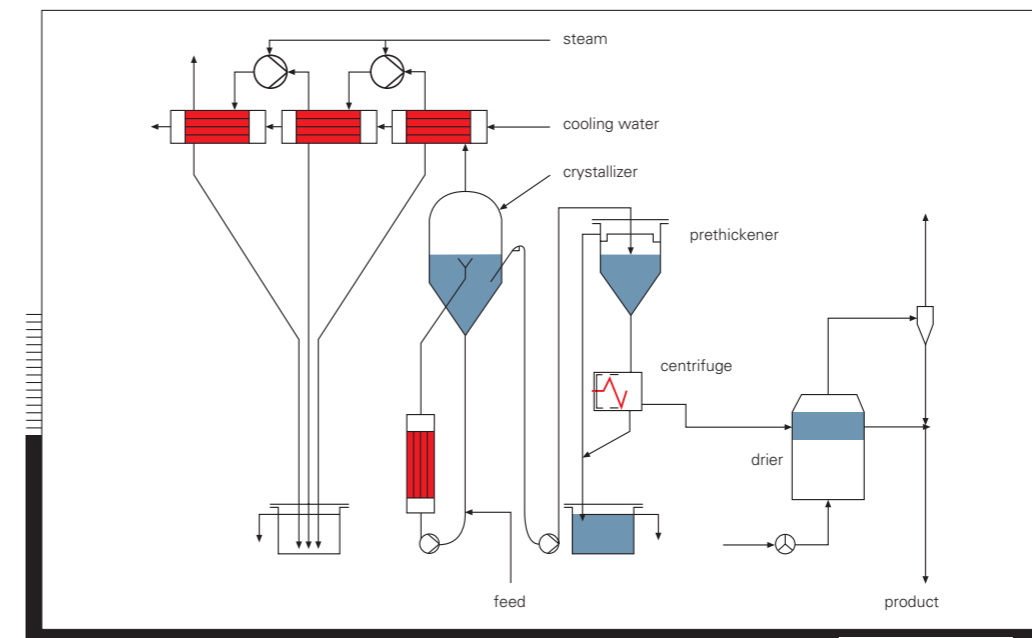
The primary advantage of the OSLO crystallizer until today is the ability to grow crystals in a fluidized bed, which is not subject to mechanical circulation methods. A crystal in an OSLO unit will grow unhindered, to the size that its residence time in the fluid bed will allow. The result is that an OSLO crystallizer will grow the largest crystals, as compared to other crystallizer types.

The slurry is removed from the crystallizer's fluidized bed and sent to typical centrifugation sections. Clear liquor may also be purged from the crystallizer's clarification zone, if necessary.

From each of these basic types of crystallizers a number of different applications are designed from MESSO engineers to fulfill the special needs of the customers.



5



4



6

4 Simplified flow sheet

5 Spin bath regeneration plant

6 Planning model of an evaporative crystallization plant (Abu Dhabi)

### Peripheral components

The crystallizer is the heart of a crystallization system, but there are several components, in the periphery, that need to be considered before the final product can be collected. The suspension from the crystallizer has to be separated, the crystals have to be dried and packed. The vapours have to be condensed and the noncondensables to be extracted by vacuum pumps.

Fig. 4 shows a simplified flow sheet of a complete crystallization plant operated on the principle of evaporative crystallization under vacuum. Depending on process considerations (crystal size, evaporative duty, etc.) one of several types of crystallizer can be installed instead of the FC crystallizer shown, including multiple-effect units.

Instead of using steam for heating (as shown), one could utilize mechanical or thermal vapour recompression. In the illustration, the vapours from the (last) crystallizer are condensed in a surface condenser; however, a mixing condenser could be chosen, instead. The suspension in the crystallizer can be withdrawn by overflow, as shown, or pumped out, using pumps with special specifications. Because suspension densities are usually between 15 to 25%wt. in the crystallizer, while a centrifuge operates best at 50 to 60%wt. suspension, the suspension is preconcentrated in thickeners or hydrocyclones.

The underflow of the thickener or hydrocyclone is sent to the centrifuge for separation. Depending on the product CSD (and to a lesser degree on the physical properties of the suspension) there is a choice between types of centrifuges: generally, the decanter and peeler are used for smaller particles, and the screen bowl and the pusher for

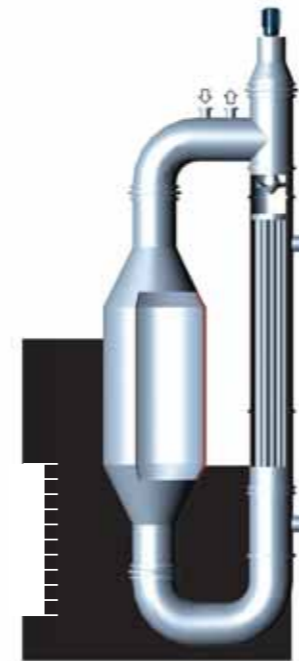
larger particles. In some cases of very small particle sizes or very fragile crystals, filters are used, instead of centrifuges. Filters, however, are usually not as efficient as centrifuges in separating the solvent from the crystals.

The small amount of residual solvent left on the crystals after the separation step, is removed in a dryer. There are several types of dryers that are used, depending on crystal size, crystal chemistry (reactive nature, tendency to decompose, oxidize, etc.), crystal fragility, and initial solvent content. The most common types of dryers used are fluid bed (stationary or vibrating), and the flash dryer.



Details from a pickling bath liquor regeneration unit

### Application examples



Loop crystallizer for bisphenol A adduct

The selection of equipment and the design of a crystallization operation is dependent on, and influenced by several process-specific factors. The following examples illustrate how these factors influence the choice of crystallizer type:

#### Surface cooling crystallization

Surface cooling crystallization will be selected if the solubility of the substance to be crystallized is strongly dependent on temperature, and if vacuum cooling crystallization cannot be chosen, e.g. the vapour pressure required to achieve the end-point temperature is too low for the plant utilities, or too expensive.

#### Melt crystallization of bisphenol A adduct

Beside a number of applications for inorganic products (e.g. Glauber's salt, carnallite) modern surface cooling suspension crystallizers are used also for melt crystallization, e.g. to crystallize bisphenol-A (BPA) phenol-adduct, the prepurification step for the melt from synthesis. The eutectic point of the melt is about 39°C, and the crystallizer is operated at 45–50°C. The BPA, which is used in the production of polycarbonate, is crystallized in a surface-cooled crystallizer from the melt, which consists of BPA, phenol and some impurities. The pure crystals are separated in centrifuges and washed with phenol. The design should recognize the tendency of the product to form incrustations on the heat exchange surfaces, there being the place of the highest supersaturation in the entire system. Polished surfaces and small temperature differences are some of the techniques used in modern designs to control the effects of this problem.

The surface-cooled crystallizer is a simple FC unit, in which the process slurry is cooled in the tube-and-shell heat exchanger in the circulating loop (loop crystallizer). Growth-type crystallizers are not commonly chosen, due to the low settling rate of the crystals, which makes fines separation at the crystallizer very difficult.



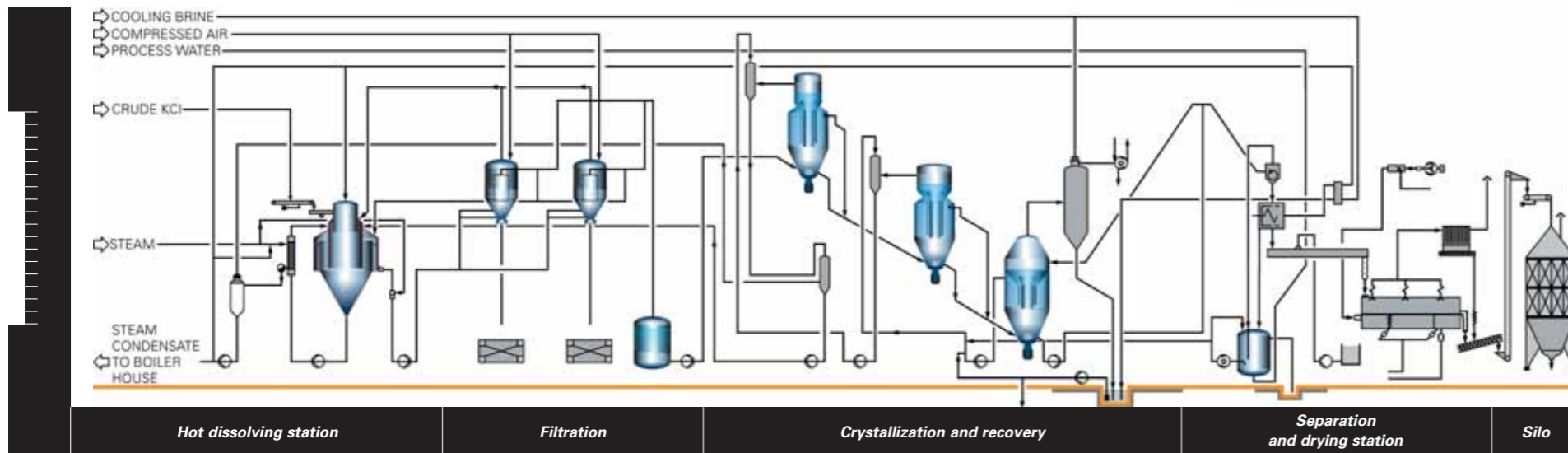
Spin bath regeneration plant

#### Vacuum cooling crystallization

Vacuum cooling crystallization is usually chosen if the solubility of the substance to be crystallized is strongly dependent on temperature, and if the vapour pressure of the solvent is high enough for this application to allow the use of conventional vacuum equipment. Vacuum cooling crystallization is the preferred cooling crystallization method for continuous operation conditions, due to the fact that the supersaturation is generated by adiabatic cooling of the solvent at the liquor level. This means that the energy is

removed from the crystallizer at a location that is far less prone to encrustations, and with a method that requires far less mixing energy input to the crystallizer slurry.





Potassium chloride refinery for ind. grade quality, triple-effect vacuum cooling crystallization

**Vacuum cooling crystallization of potassium chloride**

This example shows the recrystallization of potassium chloride in ind. grade from fertilizer quality. The crude KCl is dissolved at elevated temperatures in a recycled stream of mother liquor. The resulting solution, now saturated with potassium chloride, is fed to a multiple-stage, vacuum cooling crystallizer train. In order to fulfill the requirement of coarser crystals, the type selected is the DTB crystallizer. Fines dissolving is possible, by adding water to each crystallizer's clear liquor overflow. The number of stages is optimized on the basis of maximum heat recovery (the recycled mother liquor is reheated in condensers using the vapours leaving the hotter crystallizers).

Barometric (direct-contact) condensers are usually employed, so that the water content of the mother liquor is increased, and thus its dissolving capacity is improved. Steam is used (in separate heat exchangers) to heat the recycled, and diluted, mother liquor to the temperature required by the dissolver step, and the loop is closed by returning the mother liquor to the dissolver.

The crystals are separated in pusher centrifuges, washed and dried. The typical crystal sizes averages are 0.8 to 1.0 mm.



Vacuum evaporators for brine concentration

**Recovery of pickling bath effluent liquors**

Vacuum cooling crystallization can also be used to purify solutions, by crystallization of the solute. The pickling of mild steel sheets with sulfuric acid produces an aqueous waste stream containing ferrous sulfate and sulfuric acid. Cooling of that solution forces ferrous sulfate to crystallize as  $FeSO_4 \cdot 7H_2O$ . From the viewpoint of the mother liquor composition, this is a way to purify the solution.

At the same time, the seven molecules of water that is removed with the crystallized ferrous sulfate causes the reconcentration of the sulfuric acid. The solution thus treated can be recycled to the pickling bath. The vacuum cooling is achieved in a single-effect draft-tube crystallizer which is operated together with a high-vacuum generator (a steam ejector or chilled-water surface condenser). This modern process may be operated for a couple of months without interruptions for washouts.



**Evaporative crystallization**

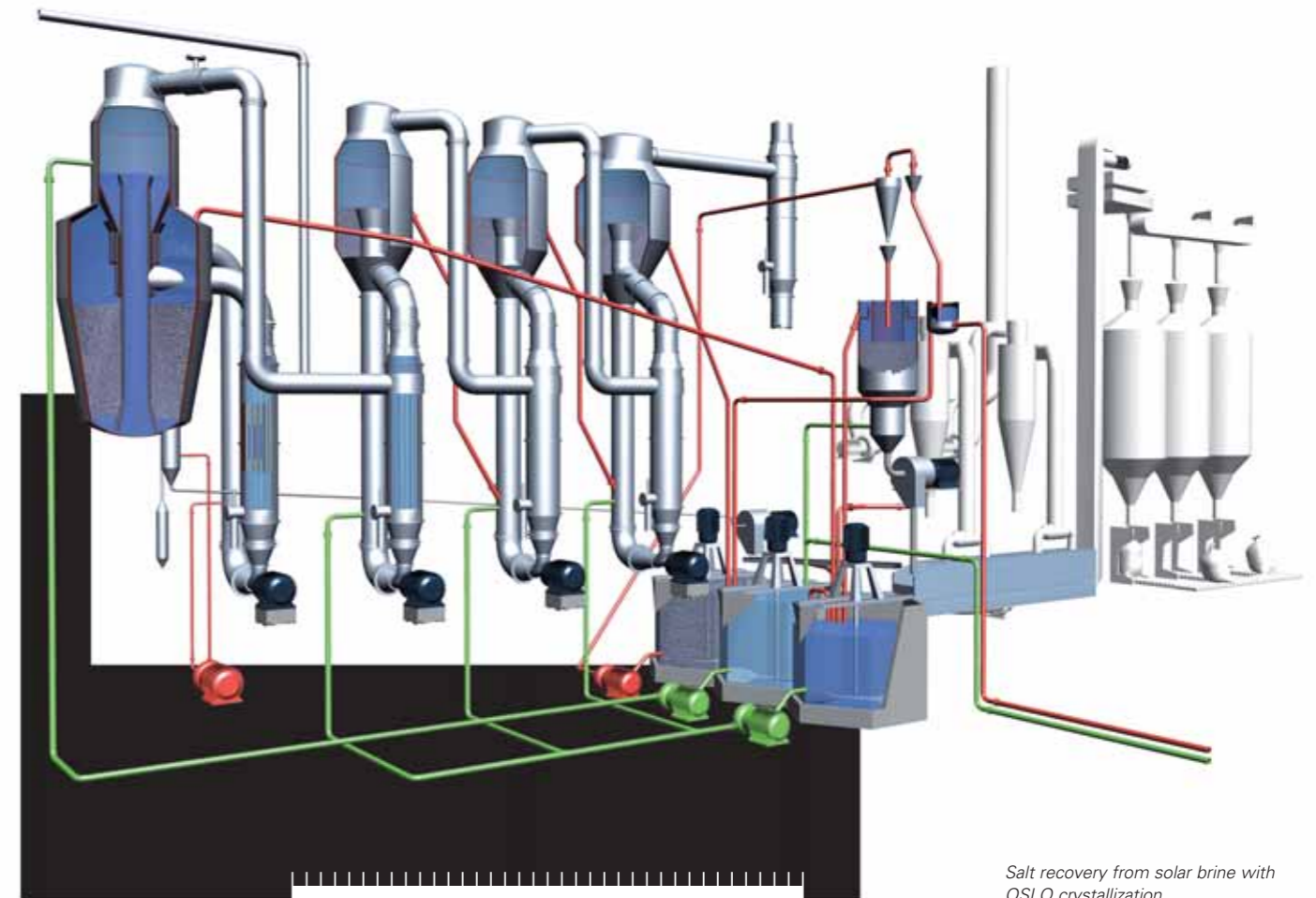
Evaporative crystallization is usually a process that is conducted under vacuum, just like the vacuum cooling crystallization. This process is chosen when solubility of the solute is nearly independent of temperature. As in vacuum cooling crystallization, special scaling problems are not a serious problem as long as boiling on the heater surface is avoided, and the special case of inverse solubility (solubility decreases with temperature) is recognized and taken into consideration.

**Crystallization of sodium chloride**

This example shows a crystallization plant for table salt, operated with concentrated brine from a solar pond. In addition to three FC crystallizers, there is an OSLO crystallizer, used by the plant to produce a fraction of its output as coarse crystals. The plant is operated as a quadruple-effect unit. The coarse crystals from the OSLO are separated on a pusher centrifuge, whereas the salt produced in the FC crystallizers is separated on screen bowl centrifuges, after being counter-currently washed with fresh feed liquor in a washing thickener. The product crystals are dried and packed. In order to

maintain the level of impurities in the system to an acceptable level, some mother liquor is removed as hydrocyclone overflow, and purged.

Some plants of this type have been supplied for the production of up to 2.5 t/h coarse (mean size greater than 2 mm) salt and additionally 10 t/h of normal salt.



Salt recovery from solar brine with OSLO crystallization

## Modern applications in environmental protection

### Flue gas desulfurization (FGD): scrubber effluent

Concentration of scrubber effluent from FGD systems in thermal power plants has been practiced for about two decades. Plants for concentration of these waste waters to dryness are in fact evaporative crystallization units, and should not be designed as simple evaporation units. Usually, FGD concentration units are combined with pretreatment facilities, such as heavy metals precipitation, in order that it may be possible to recover a brine or a product salt pure enough to be recycled in the process.



Vacuum filter for citrate extraction

This example shows an installation for the concentration-to-dryness of the liquid effluent from a flue gas cleaning system in an industrial waste incineration facility. This plant consists of a heavy metals precipitation and a double-effect evaporative crystallization unit, with two FC crystalliz-

ers supplied to recover calcium chloride dihydrate salt. The first stage is a gypsum-seeded preconcentrator, and the second stage is the calcium chloride crystallizer. The crystal product is separated on a screen bowl centrifuge, dried, packed and reused in another industrial application.

### Recovery of caffeine

When caffeine is extracted from coffee by the supercritical carbon dioxide method, a caffeine-containing waste water is produced. Evaporation, combined with a surface cooling crystallization separates this waste water into a caffeine of food grade quality, and pure distillate which can be reused for the decaffeination process. Short residence times at the higher temperatures is important in the evaporative step of this process, in order to minimize caffeine decomposition.

The process encompasses active carbon treatment used to remove impurities that influence the product colour, followed by a two-stage falling film evaporator driven by process vapours compressed to a higher pressure by a single mechanical compressor. In order to minimize residence time in the evaporators, the final concentrate is produced in a separate, smaller unit. This concentrate is finally cooled to ambient temperature in a surface-cooled loop crystallizer, to



Salt crystallizer; modified FC-type

crystallize caffeine monohydrate. The crystals are calcined to remove the water of hydration, and packed. This caffeine product is used in the manufacture of soft drinks.

### Salt from secondary aluminum slag

When aluminum scrap is molten down, the liquefied aluminum must be protected from exposure to the atmosphere to avoid its oxidation and to absorb the impurities of the scrap. This protection is provided by a layer of molten salts, preferably a mixture of potassium and sodium chloride that floats over the aluminum. This salt remains after the recovery of the aluminum, and is cast into ingots. Because of the impurities in this solid mass, left over from the scrap aluminum residue, exposure of the ingots to humidity causes evolution of various gases. The gases evolved are poisonous and explosive, and the leachate generated from dissolution of the ingot

is saturated with salts. Consequently, landfill-disposal of this waste was severely restricted in Europe during the eighties, and processes had to be developed to solve this problem in an environmentally sound way.

The slag is treated mechanically to recover most of the metallic aluminum for direct recycling, and is then fed to a cascade leaching process at elevated temperatures to achieve fast degassing

under controlled process conditions and to dissolve the salts. The degassing is made in the absence of atmospheric air, thus ensuring that the whole system operates above the gas mixture's upper explosion limit. The gases evolved are purified and fed to an incinerator that allows the plant to recover the combustion energy. After degassing, the remaining residue is separated from the salt solution by filtration on a belt filter. The filter cake containing aluminum oxide is usually sent to a landfill. The solution is fed to a single-effect mechanical vapour recompression evaporative FC crystallizer, operated at about atmospheric pressure. The resulting crystallized mixed salt product is separated on a pusher centrifuge, dried and compacted into pellets

which can be reused in the generation of the molten salt layer (in the beginning of this process).

This crystallization method can be used for the recovery of a single salt, as well as salt mixtures.

### Ammonium sulfate from the caprolactam process

Ammonium sulfate is a by-product of the synthesis of caprolactam. Multiple-effect evaporative crystallization is the well-established process to recover crystalline ammonium sulfate and market it as fertilizer. In the last few years, the fertilizer marketplace has seen an increased demand for larger crystals, and for a narrower size distribution.

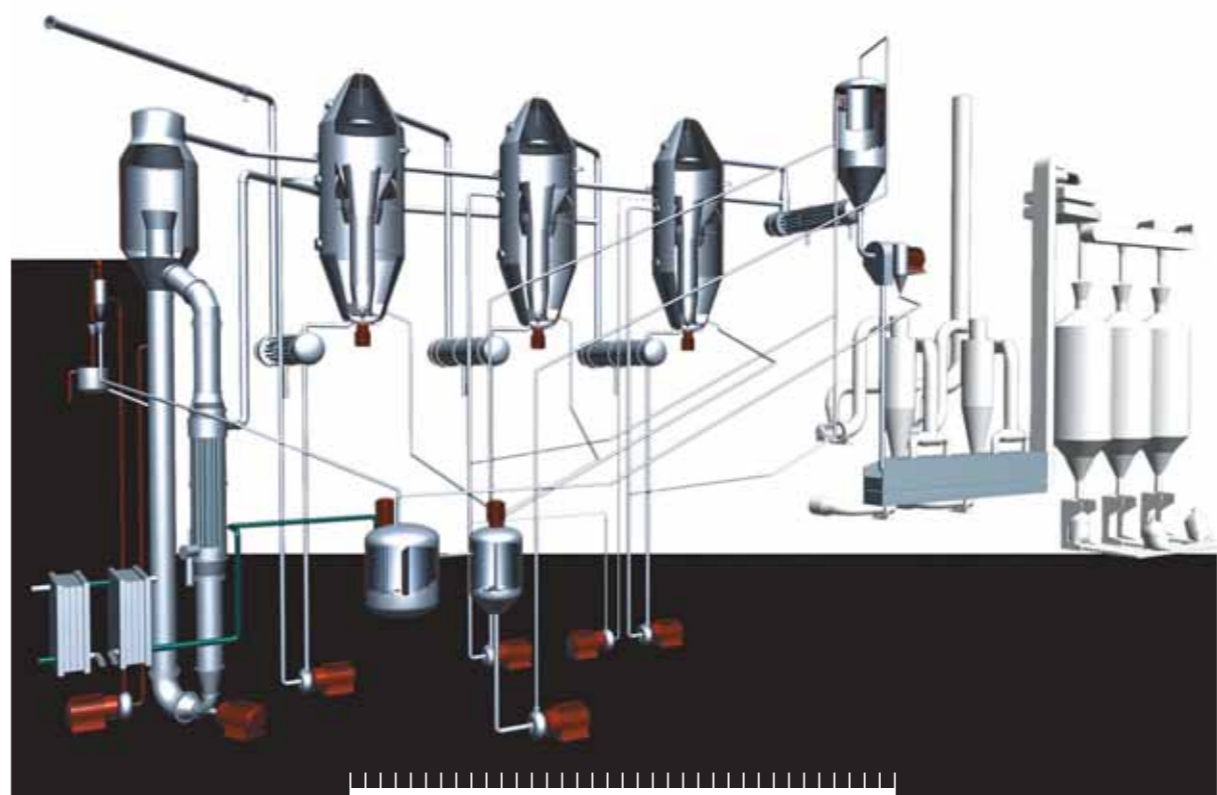


Vacuum cooling crystallizer for copperas

The example shows a triple-effect evaporative crystallization plant using DTB crystallizers for the production of ammonium sulfate of an average crystal size of about 2 mm. The solution is fed counter-currently (with respect to the steam flow sequence) in order to improve crystal growth conditions by combining the highest process temperature and highest impurity concentration. The MESSO turbulence (DTB) crystallizers use bottom-entry, custom-designed axial flow internal recirculation pumps, which provide superior mixing characteristics at a lower power requirement than common agitators. The product crystal size is enhanced by fines destruction systems. Each DTB crystallizer discharges slurry to a common slurry collection tank. The slurry is then

fed to pusher centrifuges, where the crystals are washed and separated from the mother liquor. The centrifuged crystals are dried and screened, and the undersize fraction is recycled for recrystallization.

The centrate is taken over by an aftercrystallizer (FC) to improve yield. These fine and impure crystals are concentrated by means of an hydrocyclone and the concentrated suspension is redissolved in the feed liquor. A part of the hydrocyclone overflow is taken as the liquid process purge.



Triple-effect four stage evaporation crystallization of ammonium sulphate in DTB (caprolactam process) with aftercrystallization (FC)

