Melt Crystallization

The Efficient Purification Alternative

GEA Crystallization

Preface

GEA Processing Engineering operates worldwide through local companies specializing in a wide variety of process technologies.

Recently the German based GEA Messo GmbH and the Netherlands based GEA Niro PT B.V consolidated into one operational entity: GEA Messo PT. The newly formed company will combine the two technology centers for solution crystallization and melt crystallization into one operational entity using all cross-fertilizing synergies between melt and solution crystallization. GEA Messo focusses on the recovery and purification of chemicals via crystallization.

The companies operate through a worldwide network of sales and service offices and authorized representatives, which ensures quick and professional customer support anywhere in the world.

Apart from chemical applications GEA Messo PT also provides technology for the liquid food processing industry.

Together the GEA Process Engineering companies form the largest crystallization technology supplier in the world. By combining our capabilities we can provide our clients the most complete and advanced range of concentration, purification and recovery systems available.

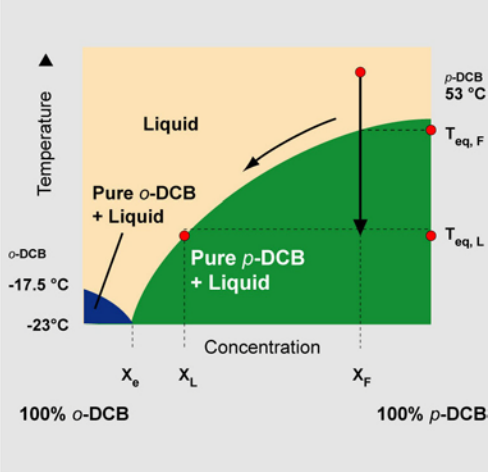
Principles of Melt Crystallization

Melt crystallization systems generally remove heat and cool the liquid melt to create a driving force for the formation and growth of crystals. Phase diagrams are used to describe the relationship between composition and temperature of a mixture at equilibrium conditions. Although industrial streams almost exclusively consist of multiple components, most organic mixtures can be described as simple binary systems. These binary systems can be subdivided into two important categories:

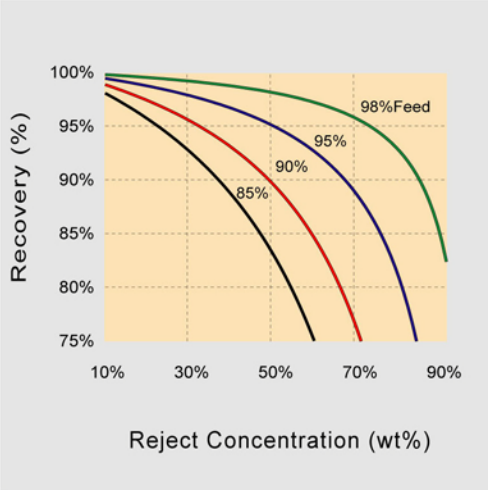
Eutectic systems, one component crystallizes as a pure solid. These systems are extremely important for purification via crystallization.

Solid-solution forming systems, in which the crystallizing solid consists of a mixture of components. These systems require multiple stages and are quite similar to the vapor-liquid separation used in distillation.

A typical eutectic mixture of p-DCB and o-DCB is illustrated in the phase diagram. Assume that the mixture has an initial melt composition of 85wt% p-DCB and 15wt% o-DCB. Upon cooling the mixture pure p-DCB crystals will be formed and the remaining liquid becomes richer in o-DCB. Additional heat removal will continue the process until the eutectic temperature and composition are reached.



Phase diagram for p/o DCB



Effect of Feed Concentration and Reject Concentration on Recovery

Crystal Purity

Pure crystals will only be obtained if they are grown very slowly at near equilibrium conditions. Higher growth rates generally result in concentrated mother liquor being included into the crystal mass.

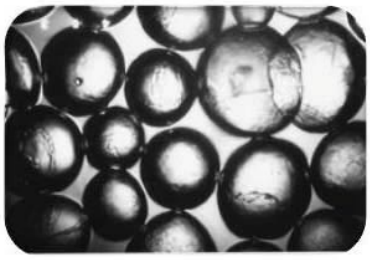
Product Recovery

The eutectic point (xe) represents the theoretical concentration limit for any melt crystallization process. Higher concentrations of impurities generally inhibit growth and can affect the crystal purity. However, slow growth rates allow pure crystal growth even near this limit. The final recovery depends on the amount of product in the original feed solution.

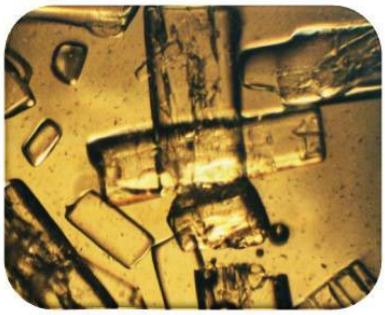
The Power of Melt Crystallization is its High Selectivity

This is caused by the fact that impurity molecules will generally not be incorporated into the highly ordered crystal lattice, provided that solid solutions do not form and that crystal growth is slow in near ideal conditions.

Analysis of more than 5000 relevant organic mixtures revealed that more than 85% of these systems exhibit eutectic behavior indicating that melt crystallization should be a feasible process option for most organic mixtures.

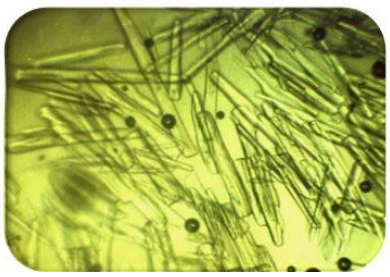


Water

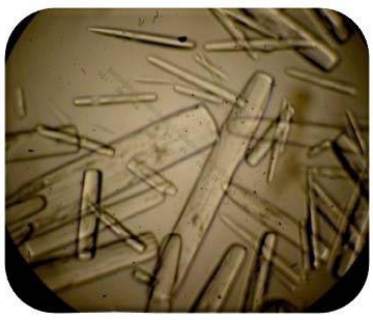


Acrylic Acid

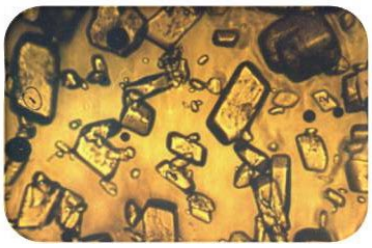
Benzoic Acid



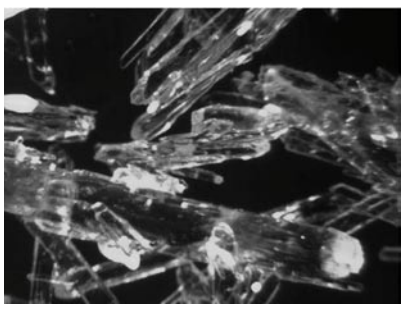
o-Phenyl Phenol



Ethyl Lactate



Paraxylene



Mono Chloro Acetic Acid

Melt Crystallization as a Chemical Process Unit Operation

The chemical industry is very much concerned with the separation and purification of chemical compounds. Impurities generally represent wasted product and cause undesirable variations to the final product quality. Specific impurities can damage catalysts and lead to failure of downstream processes.

Distillation is the industry standard for most chemical separations. It has matured into a reliable unit operation that is widely used when conditions allow the stage-wise contacting of multi-component liquid and vapor.

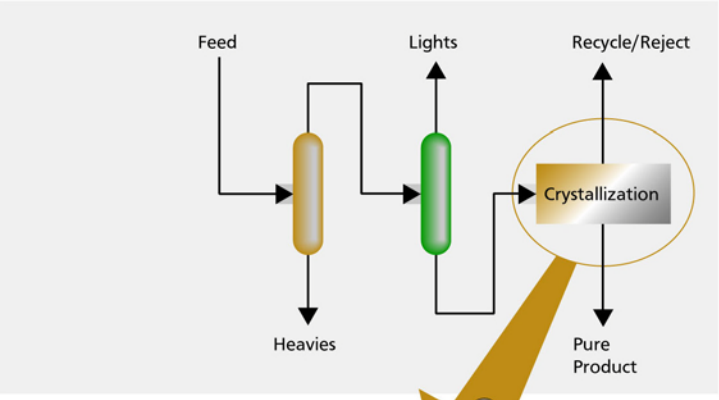
Melt crystallization is an economic and efficient alternative. It is typically used in purification applications where distillation becomes difficult:

- ♣♣Isomers with close boiling points
- ♣♣Azeotropic systems
- ♣♣Temperature sensitive substances
- ♣♣Components that tend to polymerize
- ♣♣Explosive substances

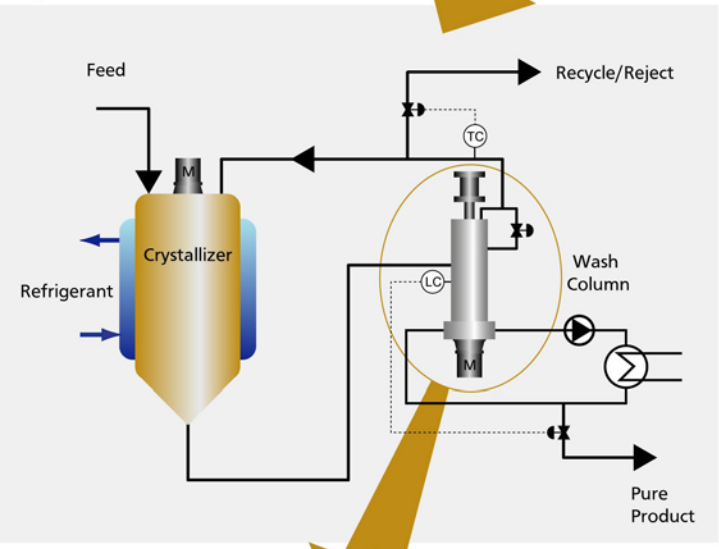
The typical eutectic system can form pure crystals of a product. This specific selectivity is not possible with any other separation technique. The crystallization process is not only applicable for new grass root plants, but ideally suited to upgrade capacity and purity of existing concentration processes such as distillation or adsorption. Small changes to existing units can significantly increase throughput by relaxing the product purity requirement of an existing process. The hybrid process completes the final purification using the GEA Messo PT crystallization process. For such de-bottlenecking projects GEA Messo PT is your partner for:

- ♣♣Increased production, recovery and product purity
- ♣♣Conversion from batch to continuous operation
- ♣♣Plant review and feasibility analysis
- ♣♣Solid-Liquid separation on existing crystallization units

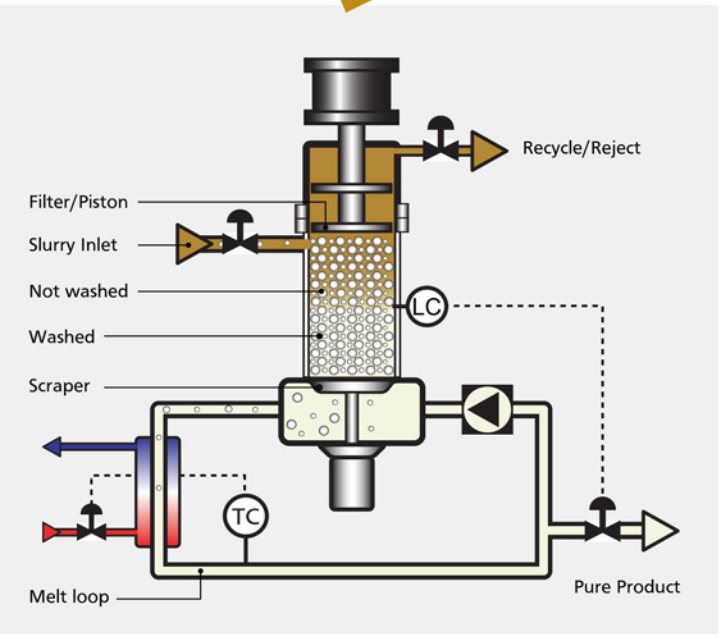
Hybrid purification process



Crystallization



Wash Column



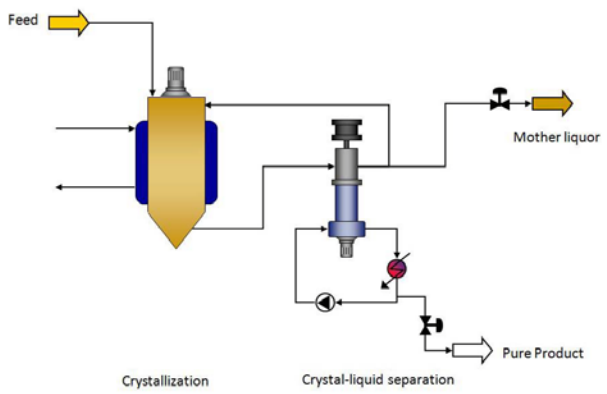
The GEA Messo PT Crystallization ProcessThe innovative alternative for attainment of pure chemicals

The GEA Messo PT Crystallization Process is a highly efficient approach for the recovery and purification of chemical components from impure solutions. Single-step crystallization and continuous operation help to provide the lowest consumption of utilities of any other commercially available crystallization process. Product purities of greater than 99.9 wt% are typically achieved. The GEA Messo PT design adheres to the following principles:

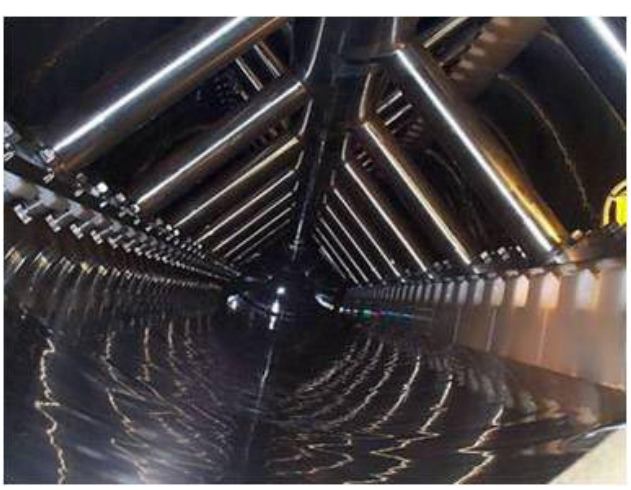
- ♣♣Suspension crystallization
  Pure crystal formation
- ♣♣Product/crystal separation using wash columns
  Efficient separation for ultra-pure product

Suspension Crystallization

The suspension-based crystallization process operates with mainly vessel type crystallizers. The large number of crystals provide a massive growth surface in a relatively small volume. Since this large surface absorbs the under-cooling of the solution, the resulting overall growth rate is extremely low. This slow, near ideal, growth allows the formation of pure crystals in a single crystallization step.



A typical suspension crystallizer may contain more than 60 billion crystals per ton of final product. This represents nearly 20,000 m2 of surface area.



Internals of a vessel crystallizer

Product Crystal Separation

The pure crystals must be completely separated from the impurities remaining in the mother liquor. The separation is accomplished within the unique GEA Messo PT Purifier.

Skid mounted melt crystallization plant for purification of enantiomers

Melt crystallization plant for purification of paraxylene

Melt crystallization plant for production of electronic grade phosphoric acid

Highly Efficient Product Crystal Separation

The heat released by this crystallization warms the surrounding crystal mass. This is a self-controlling process where the recrystallizing wash liquid will release just enough heat so that the crystals will reach the equilibrium temperature of the pure product.

This recrystallization zone, generally called the washfront, is a relatively narrow portion of the column. This washfront marks steep gradients in temperature, concentration and porosity. No wash liquid is lost to the filtrate since after completing its task as wash liquid, the new crystal product is transported together with the now warmer crystals back towards the pure wash circuit.

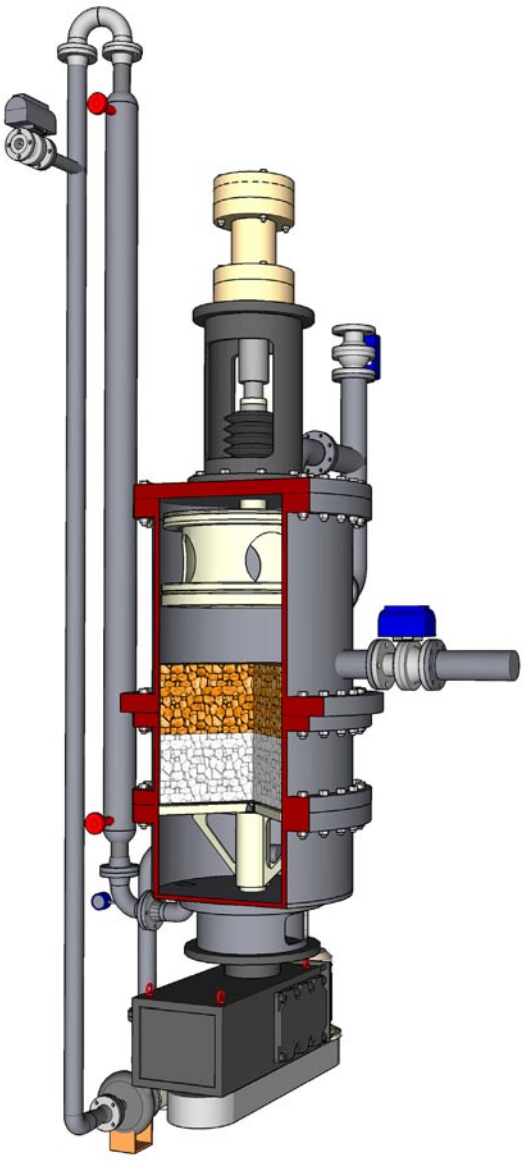
The sharp separation between the washed and unwashed portion of the crystal bed is illustrated in a wash column with transparent cylinder.

The heat released by this crystallization results in melting of the pure product. This requires an efficient washing process to remove the remaining impurities from this massive crystal surface.

In the GEA Messo PT process the product crystal separation is effected with proprietary wash column technology. The unique GEA Messo PT Purifier provides a near perfect separation between the pure product crystals and the impurity rich mother liquor. High purity is possible because 1) the crystal is already pure and 2) the counter-current wash is completed with pure melted product in a crystal bed of more than 50 cm height. This highly efficient contact between crystal and wash liquid allows sufficient time to recrystallize the wash liquid within the packed bed thereby essentially eliminating product losses from excess wash liquid.

The crystals entering the wash column are at equilibrium with the mother liquor composition from the crystallizer and are significantly colder than the melting temperature of the pure product. Most of the mother liquor is discharged through a filter. This concentrated stream of impurities can now be discharged as reject or passed to a second recovery stage.

The unwashed crystal mass is roughly 70-80% crystalline product with the remainder being the impure liquid mother liquor. As the pure wash liquid (product melt) is forced through the porous crystal bed it will effectively wash away any impurities in the unwashed part of the bed and recrystallize as new crystal product upon contacting the relatively cold crystals.



A reciprocating piston/filter draws a charge of crystal slurry into The GEA Messo PT Purifier and compresses this charge into a compact bed of crystals while allowing the mother liquor to leave through the filter. The scraper starts and the piston/filter continues to force the existing crystal bed through the column as the scraper disintegrates the bed at the opposite end of the column. The pure melted product is forced counter-current to the crystal bed flow. The porous bed provides a unique environment where the pure melt contacts the significantly colder crystals mass and results in complete recrystallization of the wash liquid. This counter-current wash flow effectively removes the impurities remaining around the crystals and returns the wash liquid as pure product crystals.

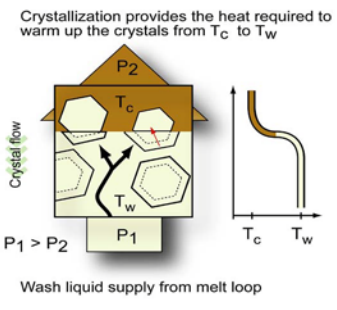
The washed crystal bed is disintegrated by a rotating scraper. The crystals are then reslurried with circulating pure melt and melted in a heat exchanger. The final product is removed through a control valve. Restricting this discharge will result in an increase in the pressure of the circulation loop.

This unique environment, not found with shorter crystal beds, allows a rather simple control strategy for maintaining product purity and eliminating loss of wash liquid.

The position of the wash front can be measured and used to control the washing pressure that determines the position of this washfront; higher pressure forces the washfront further away from the pure melt circuit.

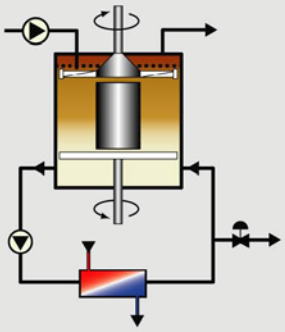
Maintaining the product purity is easy: Since the washfront does not need to be precisely located, small changes in the operating parameters, which move the wash front, have little effect on the performance of the GEA Messo PT Purifier.

Traditionally suspension-based crystallization processes use filters or centrifuges for the separation of crystals from the mother liquor. They utilize cross-flow washing of relatively thin crystal cakes (filter-cake thickness of about 1 to 5 cm) to increase the final product purity. These methods require 10 - 20% of the final product as wash liquid to achieve even moderate product purities. The excess wash liquid quickly passes through the cake and produces an extra stream of contaminated wash liquid. The crystallization section has to be sufficiently sized to treat this extra quantity of product and represents wasted resources for this inherent inefficiency.



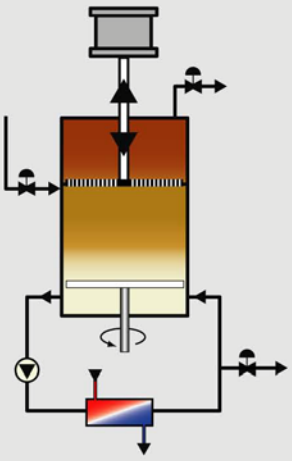
Wash Column Technologies

GEA Messo PT offers for license various wash columns that differ in the type of crystal transport mechanism. Each wash column possesses special characteristics specific to an application and GEA Messo PT can therefore assure a client of the optimal separation device for any specific application. Modular components allow a wide range of capacities.



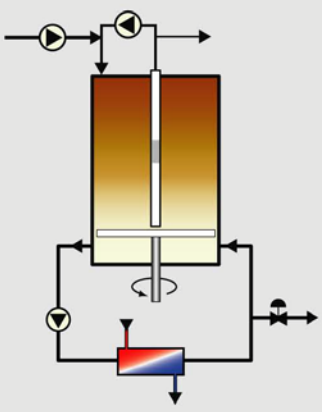
Mechanical Transport
Screw type

The screw-type, described above, is generally used for larger throughput requirements.



Mechanical Transport
Piston type

The piston-type uses a reciprocating filter piston that forces crystals through the column and is generally used on smaller capacities for more difficult separation conditions (e.g. smaller crystal size, high liquid viscosity, high temperature differences).



Hydraulic Transport

The hydraulic-type uses another proprietary filter system that allows hydraulic transport eliminating both rotating transport screw and reciprocating piston.

Pilot Plant Testing

The GEA Messo PT Crystallization Process can be applied to most eutectic solutions when the chemical compound:

Is stable at its melting temperature,

Has a liquid viscosities lower than ± 50 mPa•s

Forms crystals with reasonable filtration properties.

Initial screening is completed by comparing the product properties to our extensive database of previous test results.

Bench scale testing will provide a quick method to determine crystal habit and filtration properties using only a small volume of product. These properties give a good indication if the GEA Messo PT Crystallization Process is feasible.

The W6 pilot plant determines crystallization and separation properties on commercially relevant equipment. Scale-up is straightforward and based on standardized modular components.

- 5-15 kg/h product
- 30 liter crystallization unit
- Piston wash column
- Temperature range -60 °C to +130 °C
- Designed according to ATEX II3G IIB T3 (or T2 when heat tracing is required)
- Transportable for on-site installation in most industrial locations

Our product experience

- Acetic acid
- Acetonitrile
- Acrylic acid
- Caprolactam
- DMT
- Durene
- Ethylene carbonate
- Hydrogen peroxide
- Maleic anhydride
- 4,4’ MDI
- m-Xylene
- Methacrylic acid
- Naphthalene
- o-Phenylphenol
- p-Diisopropylbenzene
- p-Dichlorobenzene
- p-Chlorotoluene
- Phenol
- Phosphoric acid
- p-Nitrochlorobenzene
- p-Xylene
- 2,4’ TDI
- Benzoic acid
- Chloroacetic acid

Scope of Supply

GEA Messo PT designs and builds freeze concentration and melt crystallization plants for virtually every liquid food and organic product, with capacities ranging from 2,000 to 500,000 tons per year.

GEA Messo PT can provide you with the following range of services:

♣♣Feasibility Studies (Technical and Economic)
♣♣Pilot Testing
♣♣Basic Engineering
♣♣Technology License
♣♣Detailed Engineering
♣♣Supply of proprietary equipment
♣♣Supply of skid mounted preassembled installations
♣♣Project Management
♣♣Erection Supervision
♣♣Commissioning and Start-up supervision
♣♣Training of operating personnel
♣♣After Sales Services

Industrial screw type GEA Messo PT Purifier. The crystal bed fills the cylinder between the main cylinder flanges near the center of the photo.

Technology Highlights

♣♣Ultra high purities Product purities >99.999 wt-% are possible

♣♣Low energy consumption The utility cost is lower than with any competing crystallization process based on equivalent recovery and product purity. The higher efficiency of the GEA Messo PT process results from the single crystallization step.

♣♣Low capital cost The inherent efficiency and the continuous nature of the GEA Messo PT process lead to lower capital cost than for any of the competing technologies. Modular design and standard component sizes provide both easy scale-up and economy of scale

♣♣Ease of operation The GEA Messo PT process offers reliable and simple control strategies. Low maintenance and high service factor components provide years of continuous operation. Apart from pumps only low rotational speed components are applied. Bulk system volume absorbs normal operating fluctuations to stabilize production and reduce sensitivity to fluctuations in feed composition.

♣♣Small footprint Modular designs allow custom fit into existing facilities. More efficient use of equipment requires less plot space. No intermediate vessels are needed for the continuous GEA Messo PT process.

♣♣High recovery High purity crystal growth means lower reject concentrations are possible in single-stage operation. A second cold stage can boost this even further without affecting the energy efficiency since the majority of the product crystals are grown under favorable growth conditions in the larger warm-stage crystallizer.

♣♣Slurry handling With over 30 years experience in slurry handling the GEA Messo PT suspension crystallization units typically have high on-stream times.

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