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Ingénierie des Procédés- Etudes Générales
Audits Energétiques- Cogénération

CRYSTALLIZATION

SELECTION'S CRITERIA

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GENERAL

Crystallization is one of the oldest known technologies. It has been used since thousand years to make food products such as sugar, sait, etc... Despite this long history, crystallization is still an art that obeys in rare cases mathematical models or theories due to the variety of parameters (impurities, pH, viscosity, temperature ...) that are involved during this operation.

Today, crystallization is used either as a unit operation in the process (production of ammonium sulphate by reaction, sodium sulphate ...) or to treat effluents for which crystallization appears to be as the most economical solution among the technologies that can be applied (micro-filtration, reverse osmosis, drying, incineration, granulation ...).

More than one hundred single products have been or can be crystallized. These single products are normally. And especially for effluents, present with other products, which gives thousand of different solutions that have to be treated. Each case needs a thermal optimization, which multiplies again the number of answers and possibilities that a crystallization company could give to its customers for a given application.
This multitude of possibilities made the crystallization a technology that seems to be complex and not accessible or understandable to every one.

Our approach is to « demystify » the crystallization processes by using « accessible » design criteria and standard equipment. However, the selection of these criteria and the crystallization technology to be used are still obeying inviolable rules in order not to make from the selected system an unusable one or a source of unnecessary expenses (high maintenance cost, high utilities consumption, products out of specifications ...).

PRINCIPLES

Crystallization is an operation in which one or more materials are separated from a solution. We mean by solution a mixture of two or more species that fomi a homogeneous single phase *(Handbook of mistrial centralization - XX 1: Solutions and solution properties by Adam S. MYERSON)* with a certain crystal size. Shape and purity.

Such operation involves mainly two steps:

- Precipitation of the material(s).
- Control of characteristics of this (these) material(s).

* The driving force for the first step (precipitation) is the difference of solubility of the products to be separated in the solvent at the feed and the operating conditions.

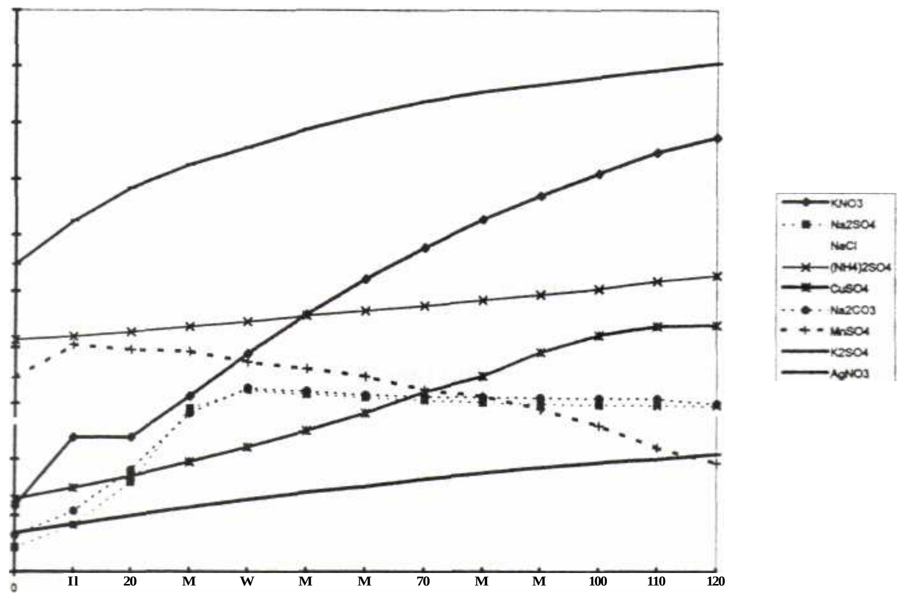
The solubility varies from one product to another, and also for products that appear similar. Fig. 1 gives the solubility for various products that are commonly crystallized. We distinguish from this figure two families of products:

« Products with « normal solubility »for which the solubility increases with the increase of the temperature (KNO_3, (NH^SO^ $AgNO_3$ ...). Products with « inverted solubility » for which the solubility decreases with the increase of the temperature (Na_2SO_4, $MnSO_4$ ...).

For each of these two families we consider two other families:

- Products with fiat solubility (NaCl, Na_2SO_4 and Na_2CO_3) at a temperature above 40°C.
- Products with steep solubility (KNO_3, $AgNO_3$, $CuSO_4$. $MnSO_4$).

Solubility curves



* The driving force for the control of the characteristics of the precipitated products are the operating conditions including temperature and temperature gradient inside the equipment. PH, concentration of impurities (initially contained in the solution or adding as such as habit modifiers), control of nuclei inside the crystallizer (fines removal and destruction), attrition....

These two driving forces and their combination lead to the selection of the adequate crystallization System to be used for a given product. Among the Systems that are presented hereafter.

TECHNOLOGIES

Depending on the solubility curve, the following technologies can be used:

* Surface cooling crystallizers
* Evaporative crystallizers
* Vacuum cooling crystallizers.

These crystallizers consist generally of forced circulation ones and allow to obtain an average crystal size between 250 and 600 microns, and normally less than 10 % of crystals smaller than 100 microns.

<u>Examples</u>

Ammonium sulfate	: 600 microns
Anhydrous sodium sulfate:	250 microns
Mono-sodium glutamate	350 microns
Calcium nitrate	: 600 microns
Glauber sait	: 500 microns
Sodium chloride	: 400 microns

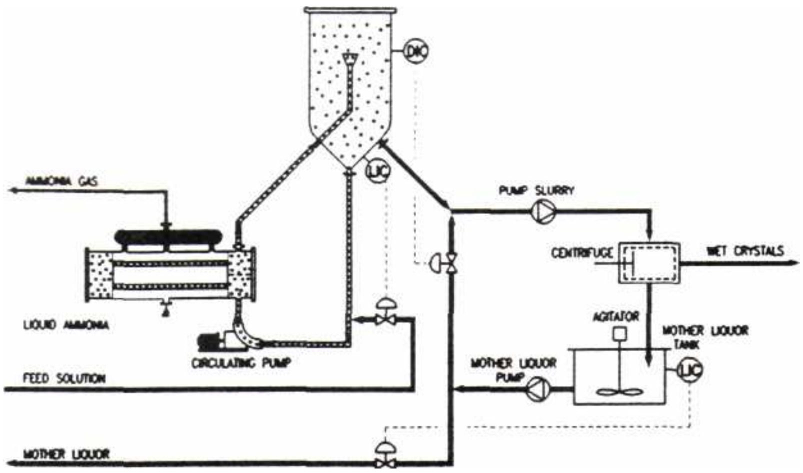
\\Tien the production of « coarse » crystals is necessary three other main technologies can be proposed:

* Crystallizer with internal recirculation
* Crystallizer with fines destruction

SURFACE COOLING CRYSTALLIZER

* Crystallizer with internal recirculation and fines destruction.

SURFACE COOLED CRYSTALUZER FOR CALCIUM NITRATE TETRAHYDRATE



It consists of a forced circulation crystallizer. The coolant can be such as ammonia, Freon, chilled water, Calcium chloride solution...

*** Typical applications:**

Solution with high boiling point for which evaporation is not economical.

- Products for which the difference of solubility between the feed temperature and the operating
  temperature is important.
- Application for which it is necessary to decrease the content of the products to be precipitated in the mother liquor (crystallization of calcium nitrate extracted out of a mother liquor from a digestion solution in order to decrease.

*** Design criteria:**

The temperature decreases across the heat exchanger and the temperature difference between the coolant and slurry circulating through the heat exchanger must be very low (less than respectively 0.5 and 10 -Q in order to achieve acceptable operating cycles. The velocity inside the tubes must be higher than 2 m s. which leads very often to multi-pass heat exchangers.

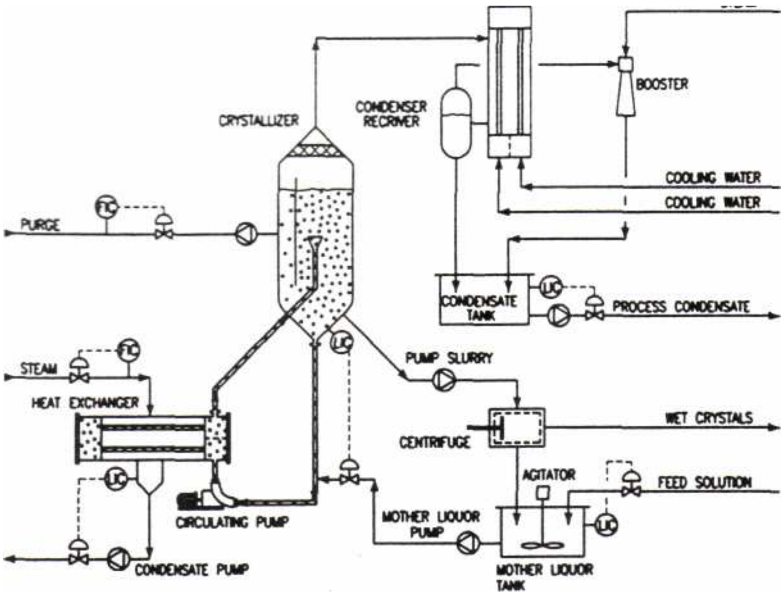
Typical products:

- Calcium nitrate, nickel nitrate, etc....
- Cupper sulfate 7H_2O. Magnesium sulfate 7 H_2O, Glauber sait,
- Sodium carbonate.

*** Main characteristics:**

Such crystallizer allows to obtain an average crystal size from 250 to 600 microns depending on the product. For mother liquors having low viscosities, it can be equipped with fines removal and destruction System, so that the average crystal size can be from 1 to 2 mm. The operating cycle for this technology is from few days to few weeks.

EVAPORATIVE CRYSTALLIZER



It consists of a forced circulation crystallizer where crystal magma is heated through a tubular heat exchanger. The heat exchanged is then released in the crystallization body producing vapors. It can be operated under vacuum or at atmospheric pressure.

* Design criteria:

The temperature raise cross the heat exchanger for this type of equipment should be between 1,5 to?-C. in order to obtain a reasonable operating cycle. The operating cycle is from few weeks to few months. The average crystal size produced is between 250 to 600 microns. This equipment can be equipped with a fines removal and destruction in order to increase the crystal size up to 1 mm.

* Typical application:

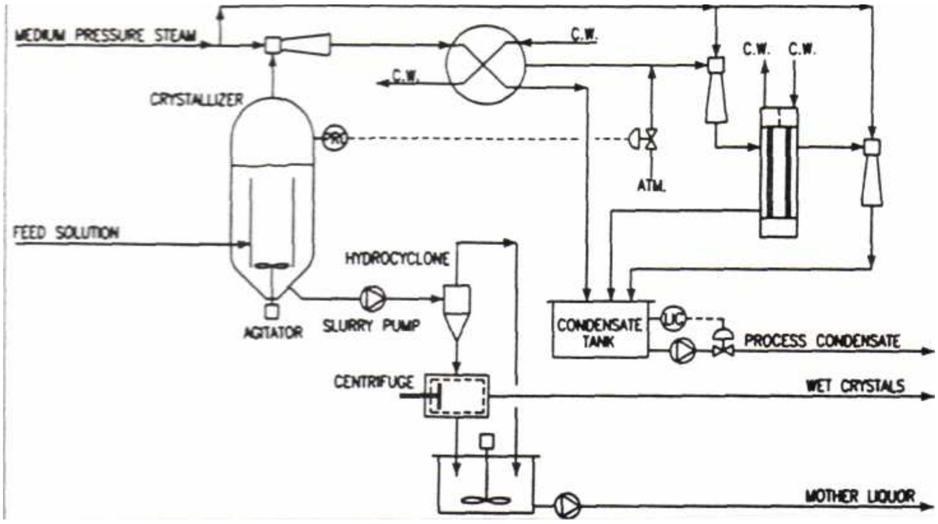
- Materials with fiat or inverted solubility,
- High evaporation is needed.

* **Typical products:**

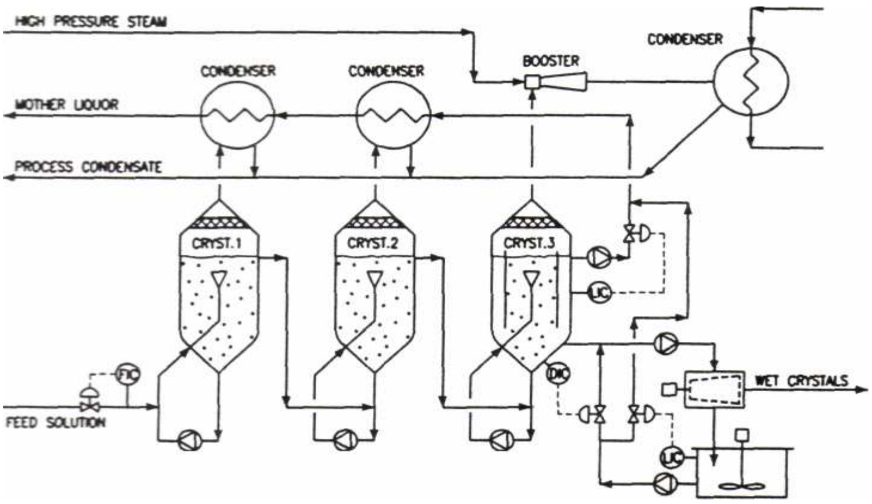
- Anhydrous sodium sulphate
- Sodium chloride
- Ammonium sulphate
- Sodium citrate
- Calcium chloride
- Citric acid.

VACCUUM COOLEVG CRYSTALLIZATION

VACCUUM COOUNG CRYSTALUZER (Example: Glauber Sait)



THREE STAGES VACCUUM COOUNG CRYSTALUZER



Such technology combines cooling and evaporation.

The crystallizer can be with internal (agitator) or external (circulation pump) circulation. It can be operated in batch or in continuous vary, simple or multiple stages.

In case of multiple stages, the mother liquor from the last effect can be used to condense the vapors from the preceding effects.

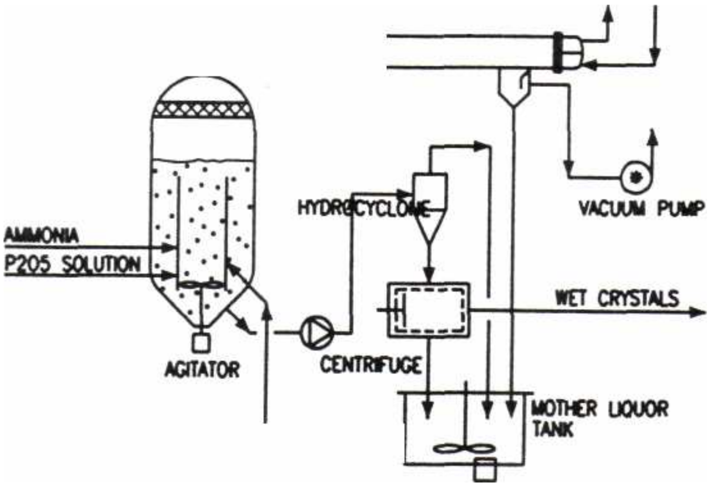
*** Typical application:**

- Glauber sait, glutamic acid. ...

CRYSTALLIZER WITH INTERNAL RECIRCULATION

CRYSTALLIZER WITH INTERNAI RECIRCULATION

(Example D.A.P/M.A.P)



*** Description:**

This type of equipment is typically used as a reactive crystallizer or as vacuum cooling crystallizer.

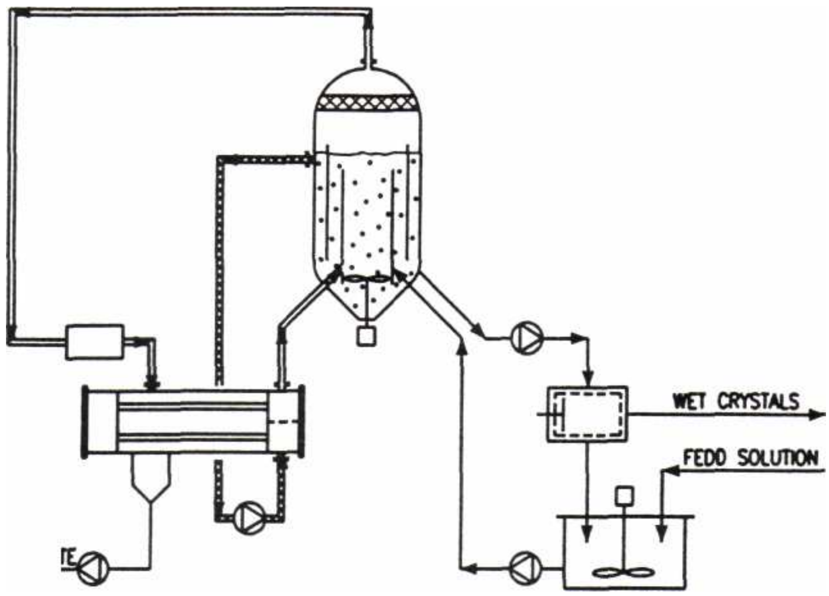
The use of an agitator as recirculator allows operating the system at a very low level of super saturation (less than 0.5°C). It Penn its to achieve a very short turn over of the mother liquor (1 to 2 minutes) and to increase the crystal size by a few hundred microns, compared to a forced circulation crystallizer.

*** Typical applications:**

- Ammonium sulfate obtained by reaction between ammonia and sulfuric acid
- Diammonium phosphate, TSF, ,,,

CRYSTALLIZER WITH LNTERNAL RECIRCULATION AND FINES DESTRUCTION

CRYSTALLIZER WITH RECIRCULATION AND FINES DESTRUCTION



* **Description:**

This type of equipment is especially used to obtain coarse crystals.

The settling zone allows to separate a big a part of fine crystals that will be sent to the dissolving System.

The dissolving System depends on the type of the solubility curve of the product.

For products with nominal solubility it consists generally of a heat exchanger using steam. An additional dissolving power can be ensured by the feed solution or an introduction of water in the System.

For products having fiat or inverted solubility curves, the dissolving power of such System is ensured by use of water.

As example, such system allows to obtain an average crystal size of 2.5 mm for ammonium sulphate and 400 to 500 microns for sodium sulphate.

OTHER CONSIDERATIONS TESTING

In many crystallization applications, data such as solubility, heat transfer coefficient, fouling factors are not available. Testing appears then as the shortest way to collect these data and optimize the design of the plant to be proposed.

THERMAL OPTIMIZATION

Most of the crystallization Systems need either steam or coolant medium (electricity). Thus the operating cost for selection of a System depends tremendously on the thermal flow sheet.

The following flow sheets can be used:

- Multiple effects units
- Multi-stages units
- Mechanical vapor recompression
- Thermo-recompression.

SEPARATION

The crystals produced during crystallization are generally separated from the mother liquor to be then dined. The selection of the separation Systems depends mainly on the crystal size and on the expected final moisture content. However, the selected separation System can affect the operating conditions of the en stallizer and therefore the definition of its performance and the construction material.

Hereafter we give an example of an application where the effect of impurities present in the feed solution influences the separation System when these impurities are not purged separately.

*** Example:**

- Feed solution 10 000 kg/h
- Composition NaCl 10 %(1 000 kg/h)
  Impurities (MgC12, Call2 ...) 0.5 % (50 kg/h)
  Water balance
- Operating temperature 83 °C

Case 1: Pusher type centrifuge will be used with 3 % final moisture content

Case 2: A filter will be used with 15 % of moisture content.

The material balance for each case is even below.

Case 1	NaCI	%	Impurities	%	Water	Total
Feed	1 000	10	10	0.1	8990	10000
Crystals	999.3					999.3
Mother liquor with crystals	0.7	10	10	32.4	20.2	30.9
~ evaporation					8969.8	8969.8

Case 2	NaCI	%	Impurities	%	Water	Total
Feed Crystals Mother liquor	1 000	10	10	0.1	8990	10000
with crystals Evaporation	961.8	22.5	10	5.9	121.5 8	961.8
	38.2				868.5	169.7 8

From these tables it appears that the operating conditions and the performances of the System will not be the same for one separation System or another.

BATCH OR CONTINUOUS

Although continuous crystallizer is more and more used, batch crystallizers still have same advantages in certain cases and especially:

- for evaporation-cooling crystallizers operating at a very low pressure,
- for very small capacities.
- for Systems designed to treat different products,
- and when the cooling range is very important.