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Crystallization Of Ammonium Sulphate: State Of The Art And New Developments

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Ammonium Sulphate has been traditionally considered a "poor" fertilizer compared to the more common urea or ammonium nitrate, due to its lower nitrogen content, i.e. 21% compared to 45% of urea. The worldwide production is approx 17 million MTPY, majority of which as a by-product, so its development is more related to the needs of other chemical production processes more than by the fertilizer market demand.

Typical processes where Ammonium Sulphate (AS) is recovered are the nylon industries, the methyl-metacrilate and the acronitrile production. Reactive and/or evaporation crystallization have been used for the recovery, depending on the internal process arrangements and/or energy situations.

The trend of the market is toward the production of the so-called "granular" AS quality, with a coarse fraction of 80%>1,8 mm, which has a higher sales return compared to standard quality but requires an improvement of the production process. This being true for both reactive and evaporative technologies, with special regard to the first one.

State of the art of ammonium sulphate crystallization

AS is produced almost exclusively in crystalline form and in its production the two major approaches are reaction crystallization and evaporative crystallization.

In reaction crystallization, such as from sulphuric acid and ammonia, the reaction that creates the supersaturation of the solute and the subsequent precipitation of crystals occurs inside the crystallizer. The heat of dissolution and of reaction, when using reasonably concentrated reactants, is sufficient to operate the process without any external source of heat to provide the necessary evaporation. The supersaturation profile and the AS crystallization kinetics, as well as the method of operation of such crystallizer, are different from those of a classic evaporative crystallizer. In an evaporative unit, the feedstock is normally undersaturated and heat is necessary to remove water in order to create supersaturation necessary for the crystallization process.

The majority of the AS crystallizers, about 80-90%, are operated in evaporation mode.

The most used types of industrial crystallizers (see Fig.1) are:

- the "Forced Circulation" (FC) type
- the "Draft Tube Baffle" (DTB) type, also called "turbulence" type
- the "Oslo" type, also called "growth" or "krystal" type

and all of them are currently used for AS production, in both reactive and evaporative applications (Wohlk and Hofmann, 1987).

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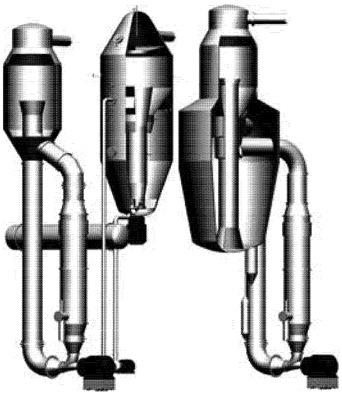

Fig.1From left to right: FC, DTB and Oslo crystallizer

Evaporative crystallization: the FC

The forced circulation crystallizer (FC) is the practical application of the MSMPR (mixed suspension, mixed product removal) crystallizer.

It is basically composed by a crystallization body and an external circulation loop whose flow rate is assured by a propeller pump, completed with a shell and tube heat exchanger.

Internal agitation is provided by an external circulator that must also satisfy the requirements of thermal exchange giving rise to the operating supersaturation.

Due to its simplicity and easiness of design and operation, it is the work horse of the chemical industry and is well suited to be arranged in single as well as multiple effects, with or without re-use of the produced vapours, both by thermal recompression (using steam driven boosters) or using mechanical compressors.

The average crystal size produced by FC's is in the order of 0,5-1,0 mm, which is rather small for Ammonium Sulphate, so such equipments are normally used for smaller operations or where other reasons are not allowing the production of a coarse product (i.e. where high level of impurities are present and/or high mother liquor is viscous). Typical examples are the handling of the purge from gas washing facilities or the treatment of purge streams from larger crystallization systems.

Evaporative crystallization: the DTB

The DTB type crystallizers are nowadays the most used equipments in large scale Ammonium Sulphate production (in last ten years more than 80% of the (NH4)2SO4 sold by the GEA companies have been DTB's).

The average crystal size (D50) produced in these units is usually larger than 2 mm. If sieving of crystals is applied after drying, a granular product of 2,4 mm, and even 3 mm as average size, can be obtained.

The draft-tube-baffle crystallizer (DTB) is an equipment designed to produce coarse and uniform crystals. It's basically consisting of a crystallization body where growing crystals suspended in their mother liquor are gently agitated by an upward draft tube circulator (propeller type), surrounded by an annular baffle from which a stream of mother liquor with fine crystals in suspension is extracted and sent to a heat exchanger in case of evaporative systems. Redissolution of such fines by heating or dilution will allow control of the crystal population and production of large size particles.

The produced crystals are extracted as a slurry and sent to a dewatering equipment, whereas the filtrate mother liquor is recycled back to the crystallizer.

The disadvantage is that, as for any system producing coarse crystals, a DTB will have a tendency to cycle in crystal size distribution. The general reason for this is that it's extremely difficult to balance the actual crystal surface in the crystallizer with the surface area required for an orderly deposition of the mass generated by supersaturation for crystal growth. The surface area is a function of the Crystals Size Distribution (CSD), that is the result of the crystal population balance as determined by such factors as the fines destruction in the external circulation loop, the nuclei generation in the internal circulation and the classified withdrawal of produced crystals.

In a DTB, when the fines destruction capacity exceeds the nucleation rate, crystals grows bigger and bigger and the available surface for de-supersaturation by growth of the existing crystals decreases to a critical point so that spontaneous nucleation occurs and a new generation of nuclei is massively formed, reducing the unit's D50. The frequency of the cycle, depending on the design and operating characteristics of the crystallizer, can range from several hours to several days (Widua et al., 2000). The cycling effect may be less noticeable in units where several crystallizers are operated and where the D50 measured is the average from all the units combined.

As it can be imagined, such cycling is undesiderable and corrective methods to minimize it have been sought by industry and designers for many years. An efficient corrective method is to measure the CSD, determine from it the available crystal surface area, and when such area decreases (the crystals are getting too large) adding to the crystallizer a certain amount of well determined fine particles ("seeds") from an external source. Few units are operated worldwide in such way, that is not only reducing cycling but also increases the average crystal size.

The degree of cycling control depends, among others, on the frequency of the CSD analysis, usually performed by sampling and sieving in a frequency from 2 to 8 hours; no on-line monitoring is known to be performed in large scale units. Given the high price incentive for large crystals, we believe that active size control will become an important issue for development.

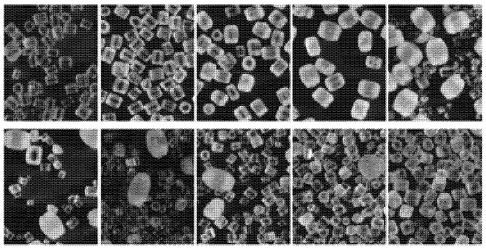

Fig.2 Cycling in DTB: variation d'=1,8-3,55 mm, average 2,5 mm, cycle time 20 h

Evaporative crystallization: the OSLO

In an Oslo crystallizer the suspension of growing crystals is carried out in a fluidized bed, where all the crystals present, except the very fines, are remaining. The fluidisation solution while passing through the external circulator is kept free of crystals by means of sedimentation at the bottom of the crystallizer and this will reduce secondary nucleation by crystals attrition, with the aim of producing coarse product. This system configuration is typical of Double Draw off systems, which provide different residence times: higher for solid with respect to that of mother liquor.

Since such circulation rate must determine at the same time the values of internal agitation, crystal bed fluidisation, supersaturation and thermal exchange duty, it must be checked carefully to fulfil process requirements. Too low circulation rate will result in low secondary nucleation , leading to bigger crystals, but at the same time will increase supersaturation that may be released forming encrustations. On the contrary, an excessive circulation rate can upset the fluidised bed and carry over crystals in the external loop, leading the system to operate as a forced circulation crystallizer.

In general an Oslo crystallizer can produce larger particle size than a DTB (in properly operated Oslo, D50 around 2,6 mm have been obtained) , but this comes at the expense of a crystallizer working volume that is about three times larger for the same production capacity. This is particularly true for ammonium sulphate, where the small density difference between mother liquor and crystals (approx 0,5 kg/l) is leading to low settling velocities for crystals, resulting in small magma density in the Oslo crystal bed.

As the market demand for granular product has increased, AS producers using Oslo have started to re-evaluate their choice and, at least in one case (Honeywell in USA), an Oslo operating as an FC has been retrofitted and converted to a DTB, increasing the produced crystal size from 1,2 mm to more than 2 mm.

	DTB	OSLO	
salt production	10.000	10.000	kg/h
supersaturation	1,80	1,8	g/l
external heating dT	8,0	1,3	°C
External circulation	900	5.600	m^3/h
internal circulation	5.600	5.600	m^3/h
velocity in settling zone	10	10	mm/s
settling area	25	154	m^2
diameter	5,7	14,0	m

Table 1 Comparison between DTB and Oslo

Reaction crystallization: the FC

Reactive FC crystallizers for AS are used only for smaller operations, since the average crystal size is around 0,4-0,6 mm. These crystals are suitable for use in mixed fertilizers, such as granulated products containing urea and AS.

The advantage of such units is the reduced energy consumption, together with a simple equipment configuration, usually based on a single stage system.

Reaction crystallization: the DTB

The DTB is usually chosen in such applications for its better mixing characteristics, which allow for improved reaction kinetics and for its ability to destroy fines, controlling the crystal population.

The two main fields of application for such systems are the following:

- the production of AS from ammonia and sulphuric acid (fresh or spent). Here a D50 between 0,9-1,4 is encountered in practice. Higher values are reachable, using more expensive design
- the production of AS as by-product from the chemical industry. Crystals of 0,8-1,0 are usually produced, although a case with a D50 of only 0,5 mm is also known.

Table 2 reports an economic comparison between evaporative and reactive crystallization, valid for a system based on DTB crystallizers, producing crystals of the same size *(Paroli,and Melches 2003)*

process	evaporative	reactive
type of unit	3 stage	single stage
capacity (MTPY)	100.000	100.000
source AS	MMA production	MMA production
annual operating cost		
steam (1,3 Eurocent/kg)	730.000	50.000
Cooling water (1,8 Eurocent/m^3)	130.000	95.000
Electric power (7,5 Eurocent/kWh)	195.000	125.000
total	1.055.000	270.000
approximate investment cost	7.250.000	5.200.000

Table 2 Comparison between evaporative and reactive crystallization

Reaction crystallization: the OSLO

Reaction crystallization in Oslo crystallizers has been applied in the past especially in the caprolactam industry, producing crystals with a D50 between 0,9-1,1 mm.

Advantages of this design is the easy of injection of the reactants in the large external circulation loop and the possibility to separate easily lighter fractions from the top of the large separating zone.

Disadvantage is the high cost related to the relevant size of the vessels.

Reaction crystallization: improved DTB application

The production of AS from sulphuric acid and ammonia in growing countries became more and more interesting in recent years, due to several local factors:

closed local markets, policy to prevent/limit import
available low cost acid from local refineries or copper smelters
available low cost ammonia, from large NH3/urea plants nearby, with excess NH3
strategic location with respect to export markets.

Thanks to this, GEA has set up two recently two of such installations, and several new plants are expected in next years, despite the incoming worldwide crisis.

In 2006 a small 150,000 MTPY package plant has been commissioned in Egypt, with the goal to produce 20 ton/h of AS with 90% crystals being between 0,5 and 3,0 mm. To reach such size a DTB crystallizer was selected. The process can be described as follows: the substantially crystal free overflow from the baffle is mixed with 97% acid and ammonia gas. The heat of reaction is removed by evaporating about 1 ton of water per ton of AS. Water is condensed and returned to the external circulation to dissolve fines, performed also by the temperature increase generated by the acid dilution and by the reaction with ammonia, always done in the same loop. Conditions have been selected to keep an unsaturation level in the loop, despite the AS formation. Special care has been put in the hydraulic design of the system in order to avoid undesired phenomena as hammering due to energic bubble generation and collapsing.

Such design demonstrated to be much more efficient than traditional reaction inside the draft tube of the crystallizer, and is able to produce crystals with aD50 between 1,2-1,4 mm. A second unit is already under construction and,, thanks to some design improvements, an increased D50 of 1,4-1,7 mm is expected.

Mixed reactive-evaporative crystallization

For systems where the reactants are not sufficiently concentrated to allow the use of single stage reaction crystallizers, a mixed concept has been developed to combine the advantages of both reactive and evaporative approach. The first step is reaction crystallization, generating water vapour that will heat one or two following steps of conventional evaporative crystallization, arranged as multiple effect system.

According to the feed characteristics, different products can be generated in the various crystallizers, combining the advantage of low energy consumption and constant crystal size of the reaction crystallization with the ability to produce larger crystals typical of the evaporative crystallization in DTB's.

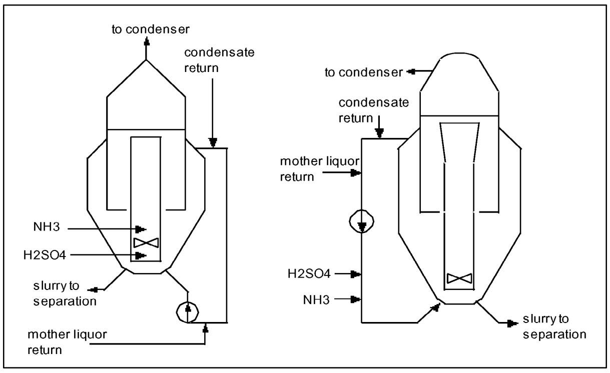

Fig.3 Reactive DTB crystallizers: "traditional" (left) and "improved" (right)

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