

THE ANALYSIS OF THE CRYSTALLIZATION PROCESS IN VACUUM SALT PRODUCTION

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Abstract: In this paper, the factors which affect the crystallization process were discussed in the vacuum salt production process. The direction of the study on increasing the crystal size was pointed out.

Key words: Vacuum salt; Crystallization; particle size

1. INTRODUCTION

In recent years, the product size and size distribution of the salt produced by vacuum evaporation system was paid more and more attention by many production enterprises. As the important quality parameters of the salt product, the particle size and uniformity of particle size distribution directly influence product purity, properties and selling price. The product which has large size and narrow distribution is easy to be filtered. The energy consumption in drying process is low. Simultaneously, the tendency of caking becomes smaller with large size crystals during the storage and transport. Even if they were agglomerated, it is easy to be broken because the unit contact points are less. Even the salt product size is so important parameter, it was not paid enough attention in the process and equipment structure in the vacuum salt production. The most attention was focused on increasing the capacity of the process and on the reducing the energy consumption. The consideration on how to provide the well crystallization environment and how to control the size of product is not

much done. Especially, the report on how to control the size of the product in the multiple-effect evaporation system is rare. The aim of this paper is to analysis the problems and to discuss the ways to improve the size of the product in vacuum salt-making process based on the crystallization mechanism, so that the attention can be paid in particle size control from all companies. The technology in controlling the product size for the vacuum salt-making process can be established.

2. THE BASIC THEORY OF INDUSTRY CRYSTALLIZATION PROCESS

The solution crystallization is the process in which solute in the solution becomes crystals. The amount of the production rate per unit solution in crystallization process is determined by the solubility of solute. The solution whose concentration is equal to solubility is called saturated solution. When the concentration is higher than solubility, the solution is called as supersaturated solution. The difference between the concentration of supersaturated solution and the saturated solution expresses

by supersaturation. The supersaturation is driving force in the crystallization process. The supersaturation has tremendous influence in the crystallization process. The level of the supersaturation decides process which occurs in crystallization process and the rate of different processes, further it influences the product size and size distribution. According to many studies^[1] the relation between statue of solution and crystallization can be expressed as Fig 1.

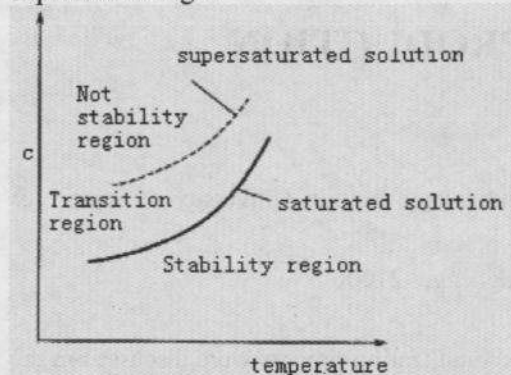


Fig.1 the solubility curve and supersaturated solubility curve

The saturated and supersaturated curve divides concentration - temperature chart into the stable region, transition region and not stable region. In the stable region, the solution is not saturated, thus the crystallization will not occur. In the transition region, the spontaneous nucleation does not occur, but if crystal is existing, the crystals will grow. In the "not stable region", nucleation will occur spontaneously. The less the stability is, the more the nuclei will be formed. Therefore in the industry crystallization process, the degree of supersaturation is the key parameter to be controlled.

Regarding relations between degree of supersaturation and the crystallization process in the industry process, the result reported by Ding^[2] pointed out that a specific system only have an explicit solubility curve, but the supersaturation curve was depended on many factors such as agitation speed, seed of crystal. In the industry crystallization process, solution should be controlled in transition region as far as possible for avoiding spontaneous nucleation and obtaining large size of product.

2.1 Crystallization Kinetics

Generally speaking, the nucleation and growth are the main processes in the

crystallization process. The nucleation and growth are simultaneous occurred in the industry crystallization process. The nucleation rate and growth rate are together called as the crystallization kinetics.

2.1.1 Nucleation

The nucleus is the core of crystal growth. If the nucleus is not existence, the phase will not change at certain degree of supersaturation, namely the solution can maintain supersaturation. The origin of nucleus mainly has three forms. First, adds the crystal factitiously, it is called adding seed crystal. The crystallization process was carried out by growing the solute on the surface of seed. The second kind of nuclei are formed from the supersaturated solution, this kind of nucleation process was called as primary nucleation. The primary nucleation is a kind of sudden process which forms small size of crystals when solution is highly supersaturated and difficult to be controlled. The third kind of nuclei is from the existed crystal. The tiny crystals which was broken down from the existed crystal, this kind of nuclei was called as secondary nucleation. Secondary nucleation process is complex and influenced by many factors which mainly include properties of crystal and operation conditions, such as mixing intensity, suspension density and degree of supersaturation.

It was found that the main factors which affect secondary rate are mixing intensity, suspension density and degree of supersaturation of the solution^[1,2,3]. The relationship between secondary nucleation rate and the factors are mostly expressed by the following equation.

$$B = K_N N^i M_T^j (\Delta C)^n$$

Where, B is the nucleation rate No. /m³s, K_N is the coefficient of nucleation rate, N is mixing intensity, M_T is suspension density, Kg/m³, ΔC is the degree of supersaturation, i, j, n are the power of the relative parameters in the nucleation equation, which can be obtained by experimental data.

2.1.2 Crystal growth

If the crystals which no matter come from the seed or secondary or primary nucleation were being in the supersaturated solution, they will grow. This kind of process is called as crystal growth. According to the

diffusion theory, the crystal growth process have three steps: (1) the crystallized solute passes through the solution layer beside the crystal surface to crystal surface by diffusion; (2) the solute arrived at the crystal surface enters the crystal face, causes the crystal size to be continuously increased and release the heat of crystallization simultaneously; (3) the heat of crystallization returns to the solution by conduction. Therefore the degree of supersaturation is the driving force of crystal growth, and directly influences the rate of the crystal growth. Usually the relationship of crystallization growth rate and the degree of supersaturation solution is represented as:

$$G = K_g \Delta C^g$$

Where G is the crystal growth rate, m/s, K_g is the coefficient of growth rate, ΔC is the supersaturation solution, kg/m³.

Because the supersaturation is the driving force for the nucleation and growth rate, the degree of supersaturation is the key factor in crystallization process. The higher the supersaturation is, the higher the nucleation and crystal growth rate are. Therefore, the degree of supersaturation has to be controlled in a proper level so that the excessive nucleation can be avoid and existing crystal growth grow.

According to the report, different sizes of crystals may have different growth rates. On the other hand, the same size of crystals may also have different growth rates. This is so-called crystal size dependent crystal growth rate and crystal growth rate disperse. About the characteristics of crystal growth rate, and the influences to crystallization process as well as product size distribution are more complicated and not discuss here.

2.2 Crystallization Kinetics of NaCl

2.2.1 NaCl Crystal Growth Rate

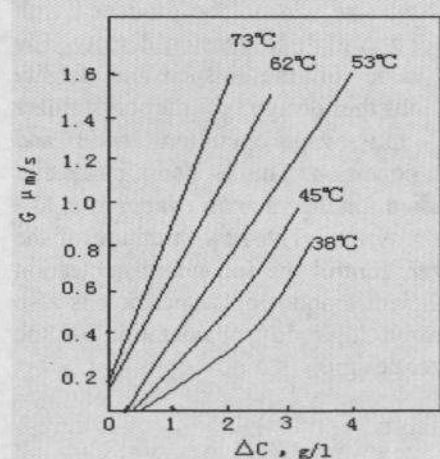


Fig.2 The growth rate of NaCl

Base on diffusion theory^[1] the crystal growth rate may be controlled by diffusion or by surface reaction. At the high temperature, the surface reaction rate can be greatly enhanced but the diffusion rate increases limitedly so that the crystal growth rate of NaCl belongs to the diffusion control. On the other hands, the process could belong to surface reaction control at low temperature. The growth rate of NaCl is given in Fig. 2. When temperature is higher than 50°C, the crystal growth rate is proportional to the degree of supersaturation as a straight line. It means that the crystal growth is controlled by diffusion. When the temperature is lower than 50°C, the relationship becomes a curve, it is a surface reaction control.

2.2.2 NaCl Crystallization Kinetics

Theoretically speaking, the solubility curve of NaCl is quite flat, and the degree of supersaturation is also small, transition area is narrow and system is easy to have nucleation. If the degree of supersaturation is small the crystal growth rate is small relatively. In order to get large size of crystals, the sufficient time for crystal growth should be provided, and crystal nucleation process should be controlled effectively.

Zhang et al.^[5] studied NaCl crystallization kinetics in the fluid bed crystallizer. The relationship between NaCl crystal growth rate and the crystal particle size, the liquid flow rate and the degree of supersaturation was experimentally obtained. The dependence of crystal growth rate G on the crystal particle size were not evidence when the particle sizes are 0.326mm to 0.693mm; The dependent of crystal growth rate G on crystal particle size L can be expressed as $G=0.2931L^{1.5967}$, when the particle size is in the range of 0.693mm to 1.768mm.

Zhou et al.^[6] studied the influences of different additive on NaCl crystal growth in the laboratory fluid bed crystallize. The results indicated that $PbCl_2$ and $K_3[Fe(CN)_6]$ could suppress NaCl crystal growth effectively even concentration of additive was very low.

According to the studies of Grootsholten^[7], the secondary nucleation rate in the MSMR crystallizer ($V=55-91L$) can be expressed as:

$$B = 1.0 \times 10^{20} (P_0 N^3 d^5)^{2/3} G^2 M_T$$

The secondary nucleation rate in the crystallizer ($V=1000-1800L$) can be express

as:

$$B = 0.023 K_N^{0.6} N^{1.2} \tau^{-1.6} M_T, K_N = 5 \times 10^{15}$$

3. THE FACTORS AFFECTING THE CRYSTAL SIZE AND CONTROLLING STRATEGY

At present^[4], vacuum salt production processes were mostly carried out with four effect force evaporator. The factors which may affect crystal size are analyzed as follows.

3.1 supersaturation and supersaturation control

The most important factor which influences crystallization is the degree of supersaturation. In a crystallization process the growth rate will increase with the increase of degree of supersaturation. High supersaturation can enhance the growth of crystal, it is a advantage for getting large size of crystal. But if the degree of supersaturation is too high and over the limit of metastable zone, the primary nucleation will occur and nucleus will be too much and the product size will be small. The key of controlling crystal size is to control the degree of supersaturation in crystallizer effectively. The degree of supersaturation in the crystallizer is decided by the balance of the rates of supersaturation creation and consumption. In the evaporation crystallization process, the rate of supersaturation creation is decided by the evaporation rate, namely the evaporation intensity of equipment. If the evaporation intensity is high, the creating rate of supersaturation will be quick and the high degree of supersaturation will be easily formed. The consumption rate of supersaturation mainly relies on the processes of spontaneous nucleation and crystal growth. If there is enough crystal surfaces and having high growth rate in the crystallizer, the supersaturation which produces by evaporation can be consumed only by crystal growth. The supersaturation will not be higher than the maximum of supersaturation, and there is no primary nucleation, large crystal is possibly obtained. If the crystal surface in the suspension is insufficient and the crystal growth is insufficient to eliminate the supersaturation which produces by evaporation, the supersaturation is high, the new nuclei will form from solution, which will consume the supersaturation. Therefore

the control of consumption and creation rate of the supersaturation will be the key technique for controlling product size in the vacuum salt production process. How to realize this balance process will be one of our important researches. But too high evaporation intensity is one important factor of too small particle size.

3.2 Influence of temperature

As shown in Figure 2, if the temperature of the crystallization is high, the crystal growth rate will be large. The temperature in each effect evaporator is over 50°C in vacuum salt production process. Therefore the crystal growth rate is under the control of diffusion. The higher the temperature is, the faster the crystal growth rate is, the bigger the product size possibly is.

3.3 Influence of suspension density

The surface area of crystals will be increased with the increase of suspension density in the crystallizer. The consumption rate of supersaturation will, therefore, be increased. The level of supersaturation will be lower in the crystallizer. The primary nucleation can be avoided effectively with high suspension density in the crystallizer. At same time, the high suspension density will increase the resident time of crystal in the crystallizer and have more time to grow and possibly can produce large size of crystals. However, too high suspension density will cause high secondary nucleation rate by collision of crystal and circulating pump, preheated pipe and circulation pipe wall, opportunity of collision between the crystal are also large. The large secondary nucleation rate can also reduce the size of product. The large crystal size can not be produced with too low or too high suspension density. The optimal value of the suspension density depends on the design of the crystallizer structure and other operation mode and operation condition. This is also a parameter to be studied for the vacuum evaporation salt production system. The new structure of the crystallizer, control the secondary nucleation with sufficient amount of suspension is also one research topic in consideration of the crystallizer design.

3.4 Influence of circulating rate

In the evaporation operation, the suitable circulating rate is very important to the control of crystal size. If the circulating rate is low, the degree of superheat of circulation fluid will increase, thus the degree of supersaturation of solution will be increased so that the nucleation on the surface of the evaporator will have more possibility to occur. It is not advantageous for the growth of crystal. On the other hand, too high circulating rate will increase the collision strength and probability of collision between crystal and crystal, crystal and wall, crystal and impeller. Therefore the secondary nucleation rate is increased. Circulating rate is very important to the salt crystal size. The suitable circulating rate which can produce the large salt crystal also depends on the structure of evaporator and operation condition of the crystallization process.

3.5 Influence of resident time

The long resident time of crystal will provide enough time for crystal growth, and the large size of crystal could be expected. According to the literature data^[8] if the average diameter of crystal is bigger than 0.4mm, the resident time should not be shorter than 1 hour. The low supersaturation and relative long residence time could be maintained by using relatively small heat exchange area and using relative large evaporation chamber. However, if the resident time is too long the secondary nucleation will be increased, the large size of product crystal could not be obtained and it can also reduce the capacity of the production. The suitable resident time is based on accurate crystallization kinetics data and be calculated on the basis of the required size of particle. As the residence time is sufficient for the crystal growth, the nucleation could be possibly too high for having large size of crystals. In this case the operation condition or other method to control the nucleation rate has to be used in the process, for example, the fines destruction technology.

3.6 Influence of process arrangement

There are several ways to arrange the multi-effect evaporation system for salt production. Based on material flow direction with the steam flow direction in the

multi-effect evaporation system, the flow arrangement could be called as co-current, countercurrent or parallel. From the point of controlling crystal size view, there is no difference between co-current and countercurrent for the process in which the pure salt solution is used. In the different effect of evaporators, the temperature is different, but the crystallization will be experienced the same way as in both processes. Therefore, the arrangement of the process does not affect the size of the crystal. But the way of the product withdraw of the system may have tremendous influence to the product size. Although countercurrent flow system can be theoretically used as it possibly obtain a large size of product size, it is randomly used in the vacuum salt production system because the product withdraw at high temperature has so many drawbacks. This paper only analyses the process of co-current and countercurrent.

The magma was transferred from I effect to II, III, IV effect in co-current process. The volume of each effect evaporator is effectively used for crystal growth. Therefore, the residence time of the crystal is longer than that in the parallel process. The large size of the product can be expected. However, under this operating condition the process operating is limited by magma density, the maximum magma density can only be used in the last effect. Therefore evaporation intensity is limited by magma density used, if the evaporation intensity is excessively high, degree of supersaturation will be high and nucleation rate will be large, the product size will be small. Generally, the evaporation intensity is high in the first effect evaporator. Therefore there possibly has large amount of small crystal if the process was not controlled well. In parallel process, each effect evaporator may think as an independent crystallizer, and easy to be controlled. If the process and crystallizer structure was design in the correct way, the expected crystal size can be obtained.

3.7 Influence of structure of evaporator

The influence of evaporator structure on crystallization process was mainly considered from the following aspects. First, the crystal should be suspended in the crystallization, particularly in the evaporation region. The enough crystal surfaces are the basic requirement to eliminate the supersaturation

produced by evaporation. Otherwise, large amount of nuclei could be formed in the evaporation area so that the size of the product crystal can not be controlled. Secondly, the possibility of the secondary nucleation has to be reduced, especially the contact nucleation caused by the circulation pump. Sometimes, fines destruction system is needed to reduce the already formed fine crystals so that the number of crystals can be reduced. It will make relative large of product crystals.

4. SUMMARIZE

NaCl crystallization in the vacuum system includes creation of supersaturate solution, crystal nucleation and growth. From the analysis above, it can be summarized that the factors which influence the product size include: the degree of supersaturation of solution, the temperature of evaporation, suspension density, the circulation velocity, the resident time of the crystals, the flow field, the structure of evaporator. In order to improve quality of salt product and to increase the size of the product the process selection, operation condition definition and crystallizer structure design are all important in the process of design and operation. It has to be paid enough attention in the future of the salt industry.

Nomenclature:

B- nucleation rate, No. /m³·s
 K_N -constant of nucleation rate
 K_g – constant of crystal growth

M_T - suspension density, Kg/m³
 G - Crystal growth rate, m/s
 ΔC - supersaturation, kg/ m³
 P_0 - power input number
 d - Impeller diameter, m
 τ - Residence time, s

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