INDUSTRIAL CRYSTALLIZATION TECHNOLOGIES AND ITS APPLICATION IN THE PRODUCTION OF SALT CHEMICAL PRODUCTS

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Abstract: The basic principle of the industrial crystallization and the control technology in crystal size and size distribution was introduced. The crystallization processes were analyzed for some products in salt chemical industry. Meanwhile the way of solving the problem was discussed.

Keywords: industrial crystallization; particle size distribution; crystal size control; salt and chemical

1 INTRODUCTION

Production of a large-scale product in salt chemical industry began in the 1950s in China. At present the comprehensive salt utilization industry has been formed with the main products of sodium hydroxide, sodium carbonate, and the product directly made from seawater chemicals (including salt lake, the underground bittern) and as well as product chain of secondary products which was produced based on the main product and its production line. The most of these products sell in the solid form in the market. The property of particles, such as particle size and its distribution, particle shape and structure, will affect the quality of products, energy consumption and the effectiveness of production process. However, consideration in the production process and equipment design was mostly focused on the balance of energy and purity requirement over the last years. The main target of the design was to increase specific production capacity and energy saving. A little was considered in the control of crystal size and its distribution. Consequently the size of particle products is generally small so that the cost of the production is high and purity is low. As the market development, the size and shape of the solid product became more and more important in product using. The technology of industrial crystallization was paid more attention for engineers. To meet the requirement of the engineers in salt chemical industry some aspects on industrial crystallization technologies and its application in the production of salt chemical products is briefly introduced in this paper.

2 INDUSTRIAL CRYSTALLIZATION TECHNOLOGIES

Industrial crystallization, as a low energy consumption and high purity product separation technology is widely used in chemical, fine chemical, pharmaceutical and active material production process. Since the 1960s, a great deal of researches has been done in the basic phenomenon and process control of the industrial crystallization process. The results have been widely used in the actual production process.

2.1 Crystallization kinetic measurement technology and its theoretical basis

Nucleation and crystal growth are the essential physical process in crystallization process and plays an important rule in industrial crystallization analysis and control. Crystallization kinetic data measurement technology was only limited to observe single crystal to measure the crystal growth rate before the 1960s. The measured crystal growth rate can not be directly applied to the real suspension crystallization processes because the phenomena in suspension crystallization are totally different with the single crystal growth. Until the 1960s, population balance theory and "Mixed -Suspension-Mixed-Product Removal (MSMPR)" model was proposed for continuous crystallization process by Randolph and Larson [1]. The relationship between particle size distribution and crystallization kinetics in continuous crystallization processes was developed. The methods were built up for measuring the nucleation and growth rate in suspension crystallization. In conditions of continuous operation with Mixed-Suspension-Mixed-Product Removal crystallizer, population balance of crystallization process can be simply expressed as:

$$\frac{dn(L)}{dL} = \frac{n(L)}{G\tau} \quad (1)$$

Where: n(L) is the population density distribution of crystal products, G is the crystal growth rate, L is the crystal size, τ is the residence time, defined as $\tau = V / Q$, V is the crystallizer volume, Q is the volume flow rate of product suspension.

After integral above equation, the crystal size distribution of continuous crystallization can be expressed as:

$$n(L) = n^0 \exp(-\frac{L}{G\tau}) \quad (2)$$

Where: n^0 is the population density when the particle size is zero.

It is defined that the changing rate of crystal number with zero size is nucleation rate, that is:

$$B^0 = \frac{dN}{dt}\Big|_{L=0} = \left[\frac{dNdL}{dLdt}\right]_{L=0} = n^0 G^0 \quad (3)$$

Under the experimental conditions, when particle size distribution of crystal products is measured, crystal growth rate and nucleation rate can be obtained.

Take natural logarithm on both sides of Eq. (2),

$$\ln(n) = \ln(n^0) - \frac{L}{G\tau} \quad (4)$$

Drawing with the crystal size L to ln(n) in semi-logarithm coordinate, a straight line is gotten, its slope is $-L/G\tau$, its intercept is $\ln(n^0)$, which can be used to obtain crystal growth rate and nucleation rate as shown in Fig. 1.

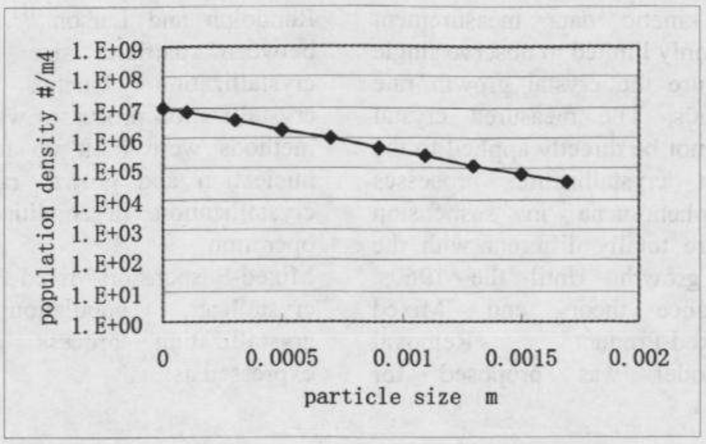

Fig. 1 The relationship between crystal size and population density in Mixed-Suspension-Mixed-Product Removal conditions

The supersaturation in crystallization processes can be altered by using different operation conditions. The different crystal size distribution can be obtained so that different growth rate and nucleation rate was obtained. The relationship between crystal growth rate and nucleation rate with supersaturation can be developed.

$$G = Kg\Delta C^{g} \qquad (5)$$

$$B = K_N \Delta C^{b} \qquad (6)$$

Generally, the crystal growth rate is not just a function of supersaturation in solution. Temperature and particle size has greatly effect on crystal growth rate. Its mechanism and expression is more complex, which can be found in literatures [2-5].

Nucleation rate is also not just a function of supersaturation. Especially in the secondary nucleation, the nucleation rate is strongly related to the suspension density and mixing intensity. Doing experiment using different mixing intensity and suspension density, secondary nucleation rate model can be obtained [6, 7].

$$B = K_N \Delta C^{b} M_T^{i} \varepsilon^{j} \qquad (7)$$

These models can be used in crystallizer design and crystal size control.

2.2 Particle size control in the continuous crystallization process

Besides pursuing high output and low consumption, the requirements of the crystal size and size distribution become important property of the product in the market. Crystal size and size distribution are important indicators of crystal products. They can affect many aspects concerning process facilities and properties of the product such as the solid-liquid separation processes, drying processes, the purity of products, products flow properties and the function of products. How to get the required particle size is the key subject to be studied in crystal technology field. There are several methods to control of product size. Different control methods can be used in different operation modes. Some methods to control the particle size in continuous crystallization process are introduced :

(1) Supersaturation control in crystallization process: supersaturation is the most important parameters in industrial crystallization process. Nucleation rate and the growth rate are directly proportional to supersaturation of solution. In partioular, the nucleation rate related to supersaturation even more evidence. If supersaturation is high, even the supersaturation is locally high, primary nucleation will occur and a large number of small particles, which makes the

product size too small, will be formed. It is necessary to control an appropriate supersaturation level in the crystallization process so that nucleation occurs with secondary nucleation. The required product size can be obtained only when the nucleation rate and growth rate match each other.

(2) Fines destruction: Despite the supersaturation in crystallization process was effectively controlled, the nucleation rate could be still higher than the requirement of the product size. The possible reason for the high nucleation rate is because that operating conditions were not properly used such as mixing intensity, suspension density. Fines destruction is often used technology to reduce the number of the crystals in the crystallization system in order to make the solute mass grow on the limited number of the crystals so that product size can be as the one required . Generally operation of fines destruction is to withdraw small crystals from crystallizer in a suitable position. Solution returns to the crystallizer after fines destructed. The method for destructing the fines can increasing the solution with fines or adding solvents to the fines solution. Because fine crystals are very small, despite eliminating a large number of crystals, their qualities are small, the output of products has been little affected. The main operations are shown in Fig. 2.

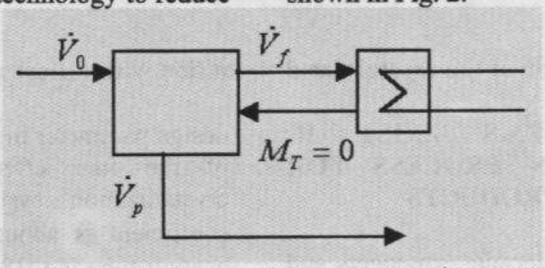

Fig. 2 The brief figure of fines destruction system

(3) Classified product removal: Classified product removal system is shown in Fig.3. Crystals withdrawn from crystallizer was classified through the size classified devices, such as the cyclone, wet-screened, gravity separation devices. The crystals whose size is larger than the separating size of the classified device will go out of the system as the product. The crystals whose size is smaller than the separating size of the classified device will return to crystallizer for further grow. However, because a large number of small crystals return to system the number of crystals which in the crystallizer will be increased. The size of crystal products will become small, sometimes even form the condition that the crystallization system can not be operated because of too many small crystal in the system. Generally speaking, only the technology of classified product removal is rarely used in the control of crystallization process. It is normally used with fines destruction.

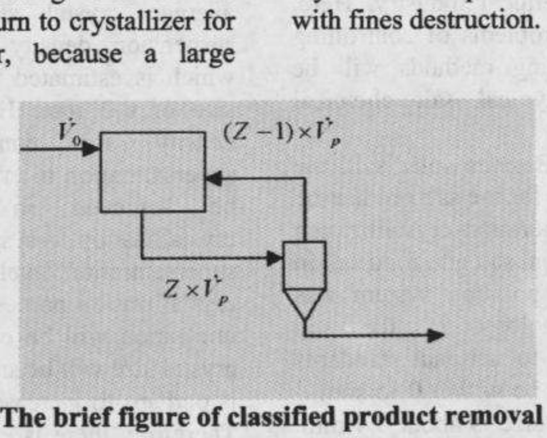

Fig. 3 The brief figure of classified product removal system

(4) Classified product removal + fines destruction: Product size can be controlled by setting fines destruction and classified product removal system in the crystallization process. The fines destruction system can be used for the crystal number controlling. The classified product removal can control the size of the crystals in the product. If the process controlled properly, the required size can be produced. Fig. 4 shows that product size distribution obtained by different control methods. Using classification product removal together with fines destruction, the crystal products with relative narrow distribution and larger particles can be gotten.

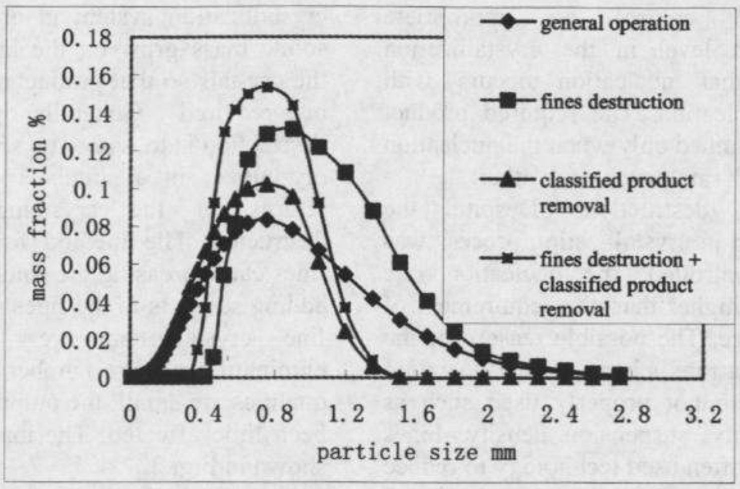

Fig. 4 Comparison of the crystal size distribution with different control technologies

3. THE PROBLEMS EXIST IN CRYSTALLIZATION PROCESS FOR SALT CHEMICAL PRODUCTS

In the past several decades, engineers and researchers have done much work on technology development of saving energy and increasing product purity. But the work on controlling crystal size was not much reported. In fact, if the product size can not reach certain requirements, the purity and energy consumption are also difficult to be controlled. It will be the most important research topics in improving product size and in establishing proper crystallization process conditions and the control methods and to apply the technology in salt chemical industry. Here, some aspects in the problems of controlling crystal size and solving methods will be introduced for the typical salt chemical products.

(1) NaCl product: Besides solar salt, the most important method for the salt production is to use vacuum evaporation crystallization which produces industrial salt and food salt in China. Four-effect evaporation system was common used technology in the salt production. According to national standards the product size has to be within 0.15 mm ~ 0.84 mm. The average size is about 0.4 mm. However, products size in the market is far away from this requirement. The main reasons about too small crystal size are possibly as follows:

Evaporation intensity: According to reports, the maximum supersaturation for NaCl crystallization is very small, only 0.05 ~ 0.1 kg/m^3 [8]. Let us to consider the general design parameter in the first effect crystallizer of the four effect vacuum evaporation crystallization system: the heat transfer coefficient is about 8360 $kJ/m^2 \cdot h \cdot ℃$, the heating tube is Φ38 × 6000, the temperature difference for heat transfer is 12 ℃ with the fluid velocity of 2 m/s through the tube. The creation rate of the supersaturation with the amount of the heat transferred is about 1.12 kg/m^3. In order to consume the created supersaturation the crystal area needed for growing those amount of NaCl is about 32463 m^2/m^3, which was estimated by the crystal growth rate of 1.2×10^{-8} m/s. In this case, the required suspension density is about 4922 kg/m^3, which was estimated with average crystal size of 0.4 mm. The suspension density is about 2488 kg/m^3, which is estimated with the average crystal size of 0.2 mm. However, the suspension density for consuming the created supersaturation in evaporator is impossible to be achieved in the real industrial crystallization system. Therefore, the supersaturation level must be reduced in the crystallization process otherwise the primary nucleation will be occurred and the product crystal size will be small. The correct solution is perhaps to increase the evaporator volume. Therefore, there is enough suspended crystal in the crystallizer to consume the supersaturation.

Crystallizer volume: The main purpose of the design for the chamber of vacuum evaporation generally is gas-liquid separation. Crystallization process has been not considered as the basis in design. As an example, let us consider a really used chamber of evaporation: the diameter of the chamber is 4.2 m, the effective liquid volume is about 62 m^3, the designed water evaporation rate is 16 t/h, and salt production is about 5.6 t/h. If the operational volume ratio of solid and liquid is 25 %, withdrawn quantity of salt slurry is about 9.7 m^3/h. Therefore. the average crystal residence time is about 6.4 h. In this case if the growth rate of NaCl is 1.2×10^{-8} m/s, and the main required product size is 0.4 mm, the residence time required by this operating case is about 3 hours. Therefore crystallizer volume generally is enough. However, it is very difficult to achieve uniform suspension in industrial crystallizer. The larger size of salt particles has less residence time. Therefore, the chamber structure should be the key factor to solve crystal growth time.

From the above analysis, too high nucleation rate is the main reason for the small size of the crystals. At the same time, the crystallizer structure will play a role on increasing the product size.

Crystal process control: Crystal size control technology is hardly used in vacuum salt production process. Although fines destruction is used to increase the product size in some salt systems, the product size can not be improved because it takes the similar effect as the classified product removal discussed above.

Therefore, in order to reach a certain product size the control technology of crystal size in NaCl production need further study.

(2) $Mg(OH)_2$ product: As a new product, product of $Mg(OH)_2$ was paid much attention by salt chemical industry. Crystallization process of $Mg(OH)_2$ is a reaction crystallization process. Normally product size is small, usually below 10 μm. It has a serious impact on the solid-liquid separation process, and difficult to control product quality.

The supersaturation of solution is relative high because of fast reaction rate in reaction crystallization process. Supersaturation was mainly consumed by forming primary nucleation, and it is more difficult to control the crystal size. The mixing process of reactants will be the most important operation for control the primary nucleation. Add seeds and the aging process will have a better effect on improvement of crystal size.

There are many salt chemical products related to particle size control problems and product quality problems. It belongs to different types of crystallization process. Different crystallization process will involve different control methods.

4 CONCLUSIONS

Crystallization process is a very complicated process. Industrial crystallization process is a process which crystal growth and nucleation occur in suspension. Therefore, the fluid dynamics which provides the external environment of crystal nucleation and growth in crystallizer has an important role on crystallization process. On the other hand, crystallization kinetics are the interior factors that determine the crystal shape and size and has a relationship with crystal material and crystallization driving force "supersaturation". If we would like to produce the solid product with the required size and size distribution, the further study on the internal links between external and internal conditions of crystallization process is necessary considered.

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