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Original Paper

A simple method to study hemihydrate phosphoric acid crystals growth process

Yong Ma[1,2,3], *Zhaoping Hu*[3,*], *Min Wang*[3], *Zhou Wang*[3], *and Ning Hu*[4]

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A simple method is introduced in this study to better understand the growth process of hemihydrate phosphoric acid crystals. Using the proposed approach, large particles (>2 *mm*) can be produced reflecting the true state of the phosphoric acid particulate system. In contrast to previous studies, the principles for the crystallization curves were divided into two regions, based on the consumption of the phosphoric acid in solution. To maintain a constant crystal growth rate, a programmed cooling requirement was needed. In this reported study, the influence of a complexing agent (EDTA) on the crystallization process of phosphoric acid was also investigated. The results of this study showed that the presence of EDTA affected the metastable zone widths, as well as the kinetics of crystal growth.

1 Introduction

With the rapid development of modern science and technology, high-purity phosphoric acid is being used for applications in many fields, including medical, environmental protection, electronics and many other industries [1, 2]. The traditional furnace manufacturing process for producing phosphoric acid limits the available quantity, so that many other methods including physical adsorption, electroosmosis, solvent extraction and crystallization have been employed to purify commercial phosphoric acid [3–5]. Of these methods, the crystallization process offers several advantages that include high separation efficiency, low operation costs, environmental acceptance all of which have been applauded by an environmentally-conscious public. At present, crystallization purification of H_3PO_4 has been the main process for production of highly pure phosphoric acid, which is demanded by the silicon tube and printed circuit board industries as an acid cleaning and corrosive agent [6].

To better understand the mechanism and design of the phosphoric acid crystallization process, it is imperative to systematically investigate both the crystal growth kinetics and the mechanism of the crystallization process. As is well known, the kinetics of crystallization are determined by measuring the crystal nucleation and growth rates, which are both functions of solution supersaturation [7]. In the kinetics study, batch cooling crystallization; affects the analysis of the distribution of crystal size using traditional-techniques, which presents difficulties in the phosphoric acid crystallization process. The reason for this is the low melting temperature of the phosphoric acid hemihydrate crystals and the facile adherence of the crystals. When separated from the mother liquor, phosphoric acid hemihydrate crystals readily melt at room temperature and barely maintain their original particle shape and size [8]. In this study, a simply, reliably method for investigating phosphoric acid crystallization is reported. Using this technique, the process of phosphoric acid crystallization can be easily elucidated. Furthermore, this new method can also be used as a reliable, practical technique to study other crystallization processes.

In recent years, extensive efforts have been expended by many researchers on the problems of phosphoric acid crystallization and much useful information has resulted [6, 9, 10]. However, the basic data that have been reported are inadequate for use in an industrial-scale phosphoric acid recrystallization process and several crucial

* Corresponding author: e-mail fortran200311310@126.com, Tel.: +86 05398766600; fax: +86 05398766609.
[1] School of Chemistry and Chemical Engineering, Linyi University, Linyi Shandong, 276000, China
[2] School of Chemistry and Chemical Engineering, Shandong University, Jinan Shandong, 250100, China
[3] National Engineering Technology Research Center for SCRF, Kingenta Ecological Engineering Co. Ltd., Linyi Shandong, 276700, China
[4] Middle school of Pengji Town, 271509, China

problems have not been adequately defined. The behavior of influential factors on the crystal growth and a reliable method for improving production are but two examples. In this reported study, the crystallization growth kinetics of phosphoric acid hemihydrate is described employing a new method and a Malvern laser particle size analyzer. In addition, the influence of a complexing agent (EDTA) on the crystallization process of phosphoric acid is also reported.

2 Experimental

2.1 Material

The analytically pure phosphoric acid and ethylenediamine tetra acetic acid (EDTA) that were used in this study were obtained from Tianjin Kemiou Chemical Reagent Co. Ltd., China and were used as received without further purification. Phosphoric acid hemihydrate crystals were obtained by condensing phosphoric acid to a concentration of 91 *wt %* and then cooling it to less than −20°C [11].

2.2 Experimental method

The laboratory study was performed in a 500 *mL* cylindrical double-jacketed glass crystallizer with an agitation speed of 100 *rpm*. To measure the crystal growth rate, the volume and the proportion of liquid-solid in the crystallization process, an additional device was included in the glass crystallizer as shown in figure 1. A photograph of a portion of the measuring tube is shown in figure 2. The measuring tube had the internal diameter of 6.5*mm*, the length of 250*mm*.

During the experiments, the liquid-solid sample (well mixed) was sucked into the injector 9 by closing valve 8 and opening the valve 10. Then valve 10 was closed; and valve 8 was opened. When the injector was pushed, the H_3PO_4 sample was transferred into the measuring tube 7, which was a double-jacketed glass tubule equipped with volume scale. In this measuring tube vessel, small crystal volume changes could be easily detected. After standing and being demixed, the crystal content of the liquid-solid sample was obtained. In cases where the sample contained a low solid content, the crystal content was resolved by repeating these operations several times until the accumulated solids content met the requirements. Additional repetitions of these operations improved the precision of the solids content measurement. Using this simple method, the solids content of the liquid could be

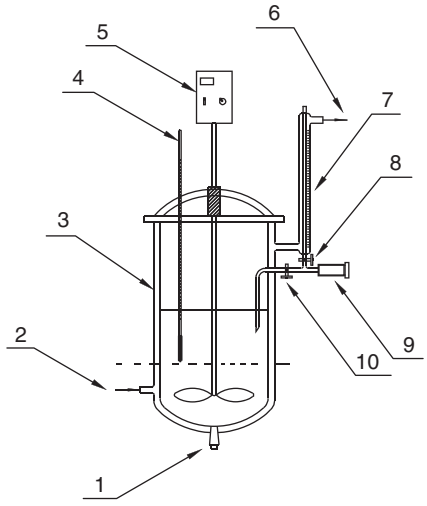

Fig. 1 Schematic diagram of the experiment setup for crystallization measurements: (1) Material outlet, (2) Cooling water inlet, (3) Crystallizer, (4) Thermometer, (5) Stirring motor, (6) Cooling water outlet, (7) Measuring tube, (8) Valve, (9) Injector, and (10) Valve.

Fig. 2 Representative portion of the measuring tube.

easily determined. Compared with traditional methods, in which crystals are separated from the liquid and then analyzed for particle size distribution, this new method offered many advantages, which allowed the crystals to maintain their original shape without melting, because of the quick and accurate measurement. Above all, this online test can reflect the natural crystallization process. Because of these advantages, this new, simple method can be applied to a wide range of crystallization processes.

It is well known that the Malvern particle size analyzer is a common particle measurement device that is widely used in many technical research fields [12, 13]. However, the Malvern particle size analyzer is limited to

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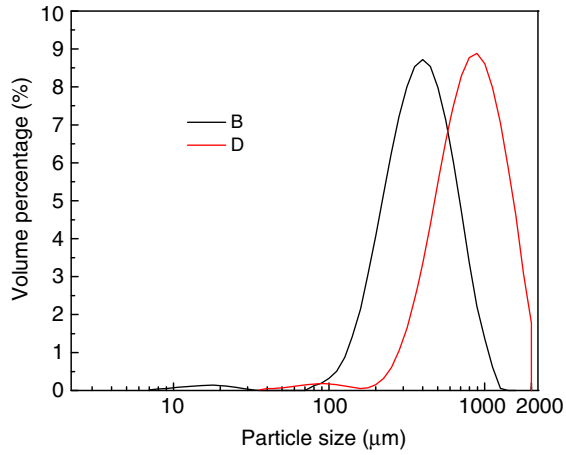

Fig. 3 Size distribution of phosphoric acid hemihydrate particles obtained by Malvern analyser after different durations of crystal growth: curve B o*h*, and curve D after 3*h*.

measuring particle groups that are less than 2 mm in size. For in the particle range of 2*mm*, the proposed method has proven to be more convenient for particle size measurement than the Malvern analyser. As can be seen in figure 3, with the Malvern S2000, line B represents the measurement results for phosphoric acid hemihydrate crystal and line D denotes the same system after 3*h* of crystal growth. In the case of the Malvern instrument, all the crystals are less than 2*mm* and line B exhibits typical good measurement results. However, the results shown in line D obtained from the same apparatus shows a different result, because particles larger than 2*mm* were present, which are beyond the measurement range of this instrument. Consequently, the measured data are incomplete and not accurately representative.

To overcome the disadvantage of the Malvern particle size analyzer, the new proposed method was used to measure phosphoric acid hemihydrate crystallization. Measurement of online particle online bulk volume was used for the larger particle ranges to depict the true state of the particle system.

3 Results and discussion

3.1 The relationship between the traditional measurement method and the new simple method

As is well known, the crystal growth rate can be described by the following expressions [14–16]:

$$G = \frac{dm}{Adt} \tag{1}$$

$$m = k_v \rho L^3 \tag{2}$$

$$A = k_a L^2 \tag{3}$$

where G represents the crystal growth rate, m is the mass of deposited solid during time t, A denotes surface area of the crystal, k_v is volume shape factor, k_a is the area shape factor, ρ is the crystal density and L is the characteristic dimension, which is assumed to be constant. So the crystal growth process can be defined by the equation:

$$G = \frac{dm}{Adt} = \frac{3k_v \rho L^2 dL}{k_a L^2 dt} = \frac{3k_v \rho}{k_a}\frac{dL}{dt} \tag{4}$$

In the case of the new, proposed method, the goal was to measure the volume change of the crystals in the mother liquor. This is defined by the following:

$$dv/dt = \frac{A' dL'}{dt} \tag{5}$$

$$dm/Adt = \frac{\rho dv}{Adt} \tag{6}$$

where v is the crystal volume, A' represents the cross-sectional area of the tube 7 (seen in figures 1 and 2) and L' denotes the change in the solid scale of tube 7. So the relationship between the two dL/dt and dL'/dt parameters can be obtained as follows:

$$dL'/dt = \frac{3Ak_v dL}{A' k_a dt} \tag{7}$$

In this form the proportionality coefficient $\frac{3Ak_v}{A'k_a}$ is a constant. That is to say that there is a proportional relationship of the crystal growth rate using the traditional measurement results and the results obtained using the new method. So, the traditional method measurement results can be obtained using this transformation. To improve the effectiveness, simplicity and ease of operation, the new, proposed crystal measurement method can be applied to many research fields.

3.2 Programmed cooling effect on crystal growth

Much effort has been expended on the phosphoric acid hemihydrate crystallization process, which has resulted in many useful literature reports that have advanced the state of the art [17, 18]. However, these previous experimental studies were conducted on only a few crystal seeds under specific conditions. Consequently, the results of these studies have limitations when applied to

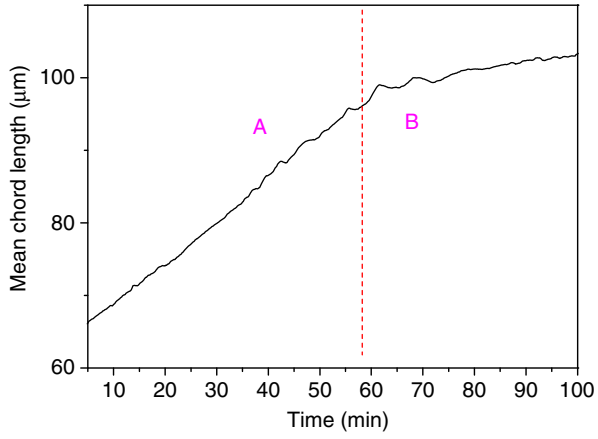

Fig. 4 Average chord length measured by FBRM during a typical crystallization process as a function of time.

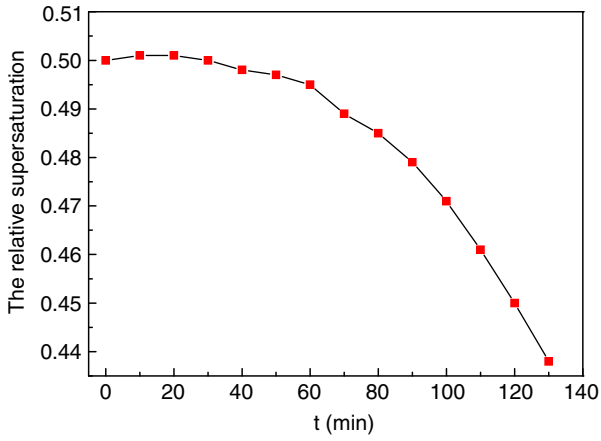

Fig. 5 Change in relative supersaturationS with crystallization time *t*.

industrial production. For industrial design and production, it is necessary to study the effect of programmed cooling on the growth of phosphoric acid hemihydrate crystals.

Previous researchers who investigated the H_3PO_4 crystal growth process noticed that the crystallization curves can be divided into several regions as shown in figure 4 [6, 8].

The reason for this behaviour has been explained as large particle crystals breaking into many smaller ones with the exception of very large crystals that exceed the measurement range. Replicating the experiments described in the literature has shown that the real reason for this result lies in the concentration of the acid in the solution is gradually reduced [8]. The solution supersaturation produced by the decrease in temperature is less than that consumed by solute precipitation. Therefore, decrease in the acid concentration results in decrease in solution supersaturation, which subsequently leads to a decrease in the rate of crystal growth, as shown in figure 5.

The results of figure 4 may be explained from the dependence of growth rate G on relative supersaturation S given by

$$G = K_G S^n \tag{8}$$

Where K_G is the growth rate constant and the exponent n represents the order of crystal growth. From this relation it follows that the growth rate is higher in the beginning than that afterwards because of decreasing supersaturation due to consumption of solute during growth in the solution of fixed volume.

To maintain a constant growth rate of phosphoric acid hemihydrate crystals, a programmed cooling method must be introduced during crystallization process, particularly in the presence of a large number of seed crystals [15, 20]. In this reported study, the phosphoric acid crystallization process began with the addition of 5 *wt %* seed crystal. To avoid the phenomenon of decreasing growth rate as shown in figure 4, the programmed cooling parameters were determined in advance. The process used in this reported study consisted of addition of 5 *wt %* seed crystal to 85 *wt %* phosphoric acid solution and the crystallization system was maintained at a constant temperature ($S = 0.5$) for $1h$. Subsequently, the concentration of phosphoric acid was measured. According to the variation of phosphoric acid solution concentration, the crystallization temperature was then adjusted accordingly to maintain the relative supersaturation ($S = 0.5$). The method used to grow the crystals entailed repeating the above steps and adjusting the crystallization temperature. The details of programmed cooling were determined in this manner.

The programmed cooling curve and the resulting volume percentage of phosphoric acid hemihydrate crystals are shown in figure 6 and 7.

It can be seen in figure 7 that there is an approximate linear relationship between the crystal volume change and the time for crystal growth. The tangent of the slope at each point on the curve represents the crystal growth rate at that time. The results indicate that the crystal growth rate in this process was constant. If the crystallization process had been monitored using Malvern particle size analyzer or a focused beam reflectance measurement (FBRM) method, results similar to those shown the line marked D (seen in figure 3) would likely have been obtained, because of the limited particle size measurement range ($<2mm$). Therefore, the results from these other test methods would result in a completely

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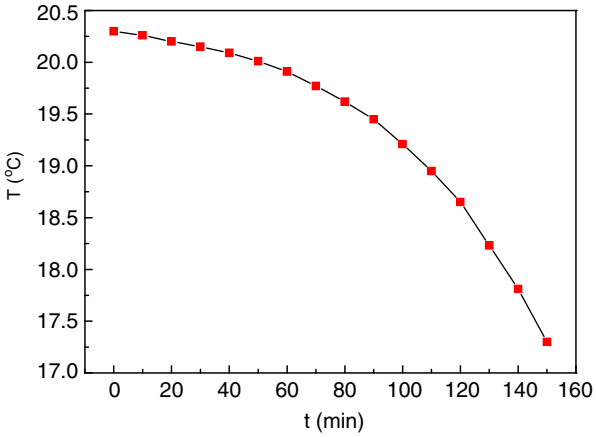

Fig. 6 Programmed cooling curve for the crystallization process.

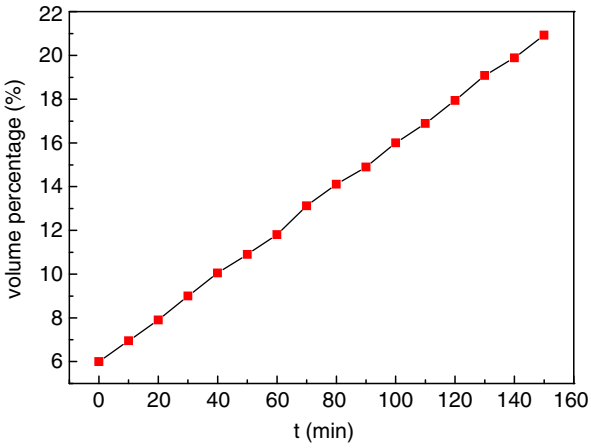

Fig. 7 Relationship between volume percent of the growth of phosphoric acid hemihydrate crystals over time.

different conclusion. The simple experimental method described in this study would be suitable for measuring many different crystallization processes especially those resulting in large crystal particles.

3.3 The influence of EDTA on the phosphoric acid crystallization process

3.3.1 The effect of EDTA on the metastable zone widths

It has been reported that the growth rate of H_3PO_4 crystals increases when the crystals are grown in solutions that include organic additives such as chelating agents (e.g. EDTA) [21, 22]. To determine which factors influence the phosphoric acid hemihydrate crystals growth process, a typical chelating agents, EDTA, was introduced. In these experiments, the laser transmission method was used to measure the metastable zone widths (MZW) [11].

Table 1 The MZW of 85 wt % phosphoric acid with EDTA.

	ΔT_{max}/K			
EDTA wt %	0.5 K/h	1.0 K/h	2.0 K/h	4.0 K/h
0	1.98	2.15	2.29	2.73
0.1	2.24	2.45	2.66	3.22
0.5	2.43	2.74	2.99	3.49
1.0	2.61	2.97	3.15	3.72
2.0	2.70	3.14	3.22	3.83

The MZW of various concentrations of phosphoric acid are shown in 1.

As can be seen from these results, the presence of EDTA enlarged the MZW of the phosphoric acid solution. Within a specific concentration range, a higher the EDTA concentration in solution will produce a larger MZW. Reports in the literature have detailed how the chelating action of EDTA significantly enhances the MZW [23].

3.3.2 The effect of EDTA on the crystal growth kinetics

In comparison to the crystallization conditions without EDTA, the presence of this chelating agent appears to an increase the growth rate of H_3PO_4 crystals. To compare the effect of the presence of EDTA under identical growth conditions, we introduce an effectiveness parameter K for crystal growth in the form

$$K = \frac{G'}{G} \tag{9}$$

Where G and G' denote the growth rate in the absence and presence of EDTA, respectively. The experiments were conducted under the conditions of a constant relative supersaturation ($S = 0.5$), doping with 5 *wt %* seed crystal in 85 *wt %* phosphoric acid solution. All growth rates were measured using the proposed simple measurement method. The experimental results are shown in figure 8.

As is shown in figure 8, the growth rate was faster with EDTA in solution than without the EDTA. Within a set concentration of the chelating agent (< 1 *wt %*), when the concentration of EDTA was increased, the crystal growth rate will increased. Moreover, compared to the previous crystallization conditions, the EDTA increased the growth rate, but also increased the size of the

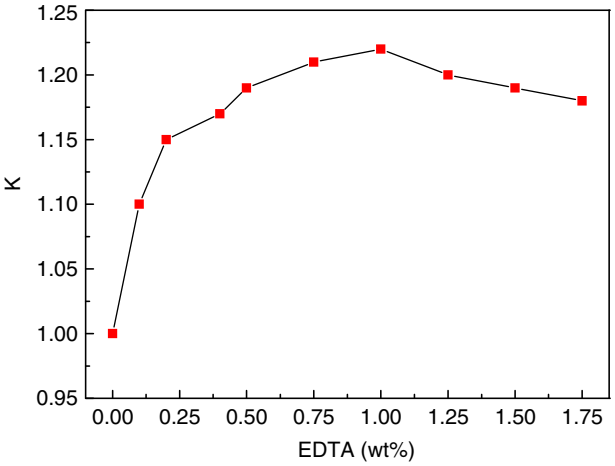

Fig. 8 Dependence of effectiveness parameter *K* for growth on concentration of EDTA.

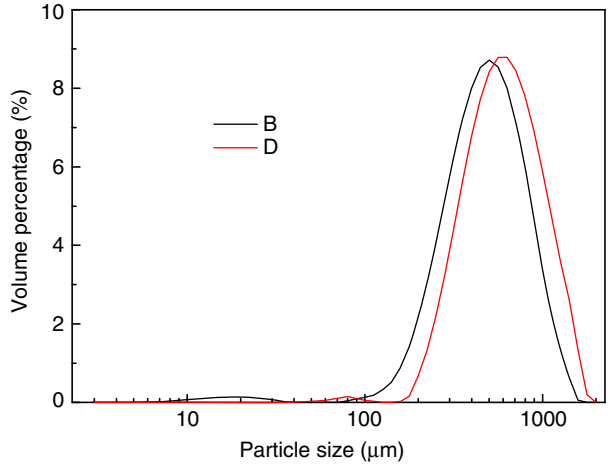

Fig. 9 Crystallization results for addition of EDTA: curve B without EDTA, and curve D with 0.01 *wt* % EDTA.

crystals. Using the Malvern particle size analyzer (Malvern S2000), the results of the experiments conducted under identical conditions are shown in figure 9. As can be seen, addition of EDTA to solution resulted in larger hemihydrate crystals than a similar experimental solution with no EDTA.

The reason for this result has been studied by many researchers [21, 22]. It can be explained that EDTA is a strong complexing and hexadentate chelating reagent. So it is easy to form coordinate bonds with ions, reduce their chemical activities in solutions and decrease the content of ions incorporated into the resulting crystals. The chelating reagents can mitigate the adverse effects of rapidly grown crystals. This is most likely the reason why doping with EDTA can provide beneficial effects on the MZW, and the growth process of the rapidly grown crystals.

4 Summary and conclusion

A new, simple method was developed and is reported in this study to investigate hemihydrate phosphoric acid crystals growth process. Compared with conventional analysis instrumentation (Malvern and FBRM), this new measurement method allows large generated particles ($>2mm$) to be measured; therefore, reflects the true state of the particle system. In contrast to previous understandings, the crystallization curves can be divided into several regions where large particle crystals break into smaller ones as reported in the literature, but also reflect the consumption of phosphoric acid from solution. To maintain a constant crystal growth rate, a programmed solution cooling rate was required. The influence of addition of organic additives (EDTA) on the phosphoric acid crystallization process was also investigated. The experimental results showed that the presence of EDTA in solution affects the metastable zone widths and, the kinetics of crystal growth. The experimental results suggest that EDTA enlarges the MZW of phosphoric acid. Within a set concentration range, a higher EDTA concentration in solution will produce a larger MZW. These results indicated that addition of EDTA to the crystallizing system can produce larger H_3PO_4 crystals than an identical system without EDTA.

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Key words. metastable zone widths, crystal growth kinetics, phosphoric acid, EDTA, EDTA.

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