

Short communication

## A note of the purity of crystals produced in batch suspension crystallization

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### Abstract

Potassium chloride, potassium hydrogen phthalate and succinic acid were crystallized from aqueous solution by unseeded batch crystallization. The agglomerates produced under high loading conditions were purer than the less agglomerated crystals produced under low loading conditions for all the substances examined. This is because agglomerates are composed of small primary crystals of high purity. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Crystal purity; Agglomerate; Inclusion; Crystallization

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### 1. Introduction

Batch suspension crystallization is widely used as an industrial technique for producing crystalline particles. The purity of product crystals is lowered by the mother liquor adhering to the crystal surfaces and trapped in the crystals. The adhering mother liquor can be removed by washing, if the crystalline particles are large enough. However, the trapped liquor (inclusion) is impossible to be removed. Therefore, for crystallization, it is important to seek conditions that avoid inclusion formation.

Inclusions formed during suspension crystallization can be divided into two types with respect to the mechanism of formation. Formation of type-I inclusions (Fig. 1) is accompanied by the damages of crystal surfaces [1] or by macro-step generation [2–4] with temporal crystal growth enhancement triggered by mechanical impacts [2] or adhesion of fine crystals onto the crystal surfaces [3]. While, type-II inclusions are of mother liquor trapped between the primary crystals composing agglomerates (Fig. 1). Funakoshi et al. [5] observed that the purity of *m*-chloronitrobenzene agglomerates becomes lower as the number of

constituent crystals is increased because of the increase of the number of type-II inclusions.

Saito et al. [6] reported that the total volume of inclusions per crystal was roughly expressed to increase in proportion of the fourth power of crystal size. However, there seems to be a slight difference in the inclusion volume, depending on the suspension condition. According to Ehara et al. [7] the inclusion ratio in sodium chloride crystals produced from a batch crystallizer is smaller than that from a continuous crystallizer. However, the cause of the difference was not discussed in the paper.

The purpose of the present work is to examine the relation between suspension condition and purity of product crystals. The purity of agglomerated crystals can be different than the observation of Funakoshi et al. [5]. The purity of agglomerates must not be always lower. High loading batch crystallization can produce high purity agglomerate consisting of small primary crystals of high purity.

### 2. Experimental

Three substances (potassium chloride, potassium hydrogen phthalate and succinic acid) are crystallized batchwise from aqueous solution under low and high loading conditions. Loading indicates the strength of supersaturation condition and it is defined as the yield of crystals. The conditions of crystallization are shown in Table 1. Cooling

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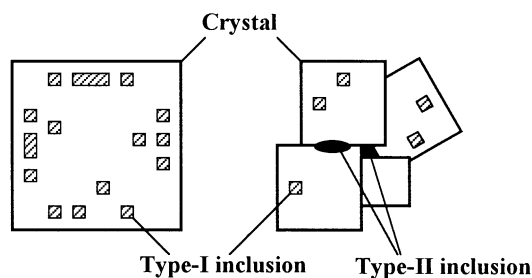


Fig. 1. Schematic drawings of type-I and type-II inclusions.

crystallization was performed using a 2 l agitation vessel as described in detail in a previous report [6]. For potassium hydrogen phthalate system and succinic acid system, high loading was achieved by increasing the temperature difference between the initial and final states. Only for potassium chloride system, high loading crystallization was achieved by evaporation, because of a small temperature coefficient of solubility. For evaporation, a 1 l flask in a mantle heater was used as crystallizer.

Product crystals were separated from the final suspension by vacuum filtration using a membrane filter and dried in an

Table 1  
Crystallization condition

	Crystallization method					
	Cooling (potassium chloride)	Evaporation (potassium chloride)	Cooling (potassium hydrogen phthalate)	Cooling (potassium hydrogen phthalate)	Cooling (succinic acid)	Cooling (succinic acid)
Crystallization time (h)	0.25	5.5	0.47	0.27	0.17	0.32
Stirring rate (rpm)	250	1 <sup>a</sup>	250	250	250	250
Saturated temperature (K)	343	300	298	343	303	338
Starting temperature (K)	346	300	299	345	306	342
Terminal temperature (K)	293	–	284	293	290	293
Final suspension density	0.038	0.20	0.0050	0.11	0.015	0.15

<sup>a</sup> Stirring rate was increased as the number of suspended crystals increased.

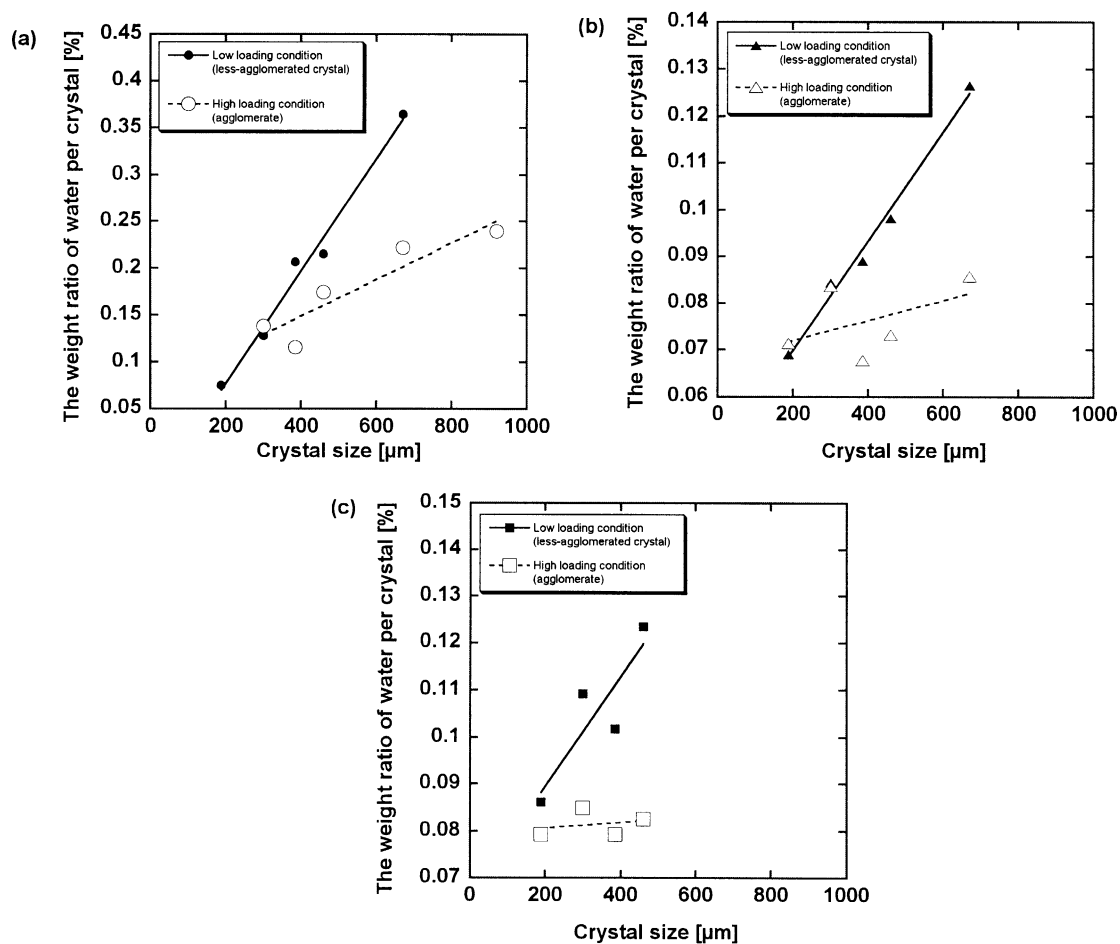


Fig. 2. The relation between the weight ratio of water per crystal and crystal size: (a) potassium chloride; (b) potassium hydrogen phthalate; (c) succinic acid crystals.

oven for several days to remove water from mother liquid adhering on the crystal surfaces. The crystals were classified into several size groups by sieving. The arithmetic mean of the successive sieve openings was used as a representative size of each group of crystals. The weight of water contained in crystals was measured with a Karl Fischer aquameter (DL18, Mettler Toledo, KF reagent: Hydranal Composite 5, No. 34805, Riedel de Haën, solvent: Solvent FM, No. 34853, Hayashi Pure Chemical) and then the weight ratio of water contained in crystals was calculated.

### 3. Results and discussion

The weight ratio of water contained in potassium chloride crystals was plotted in Fig. 2a as a function of the crystal size. Closed circles (●) in the figure show the water ratio for crystals produced under the condition of low loading. Since the crystals are less agglomerated, the detected water is mainly of type-I inclusions. The ratio increases as the crystal size is increased, because of collisions of crystals with other crystals, impeller and the crystallizer wall, which are causes of type-I inclusion formation [2], occurs more frequently in larger crystals [6]. On the other hand, the products obtained in the high loading crystallization, which are mainly agglomerates. The water ratio in these agglomerates (○, Fig. 2a) does not come only from type-I inclusions but also from type-II inclusions. It also increases as the agglomerate size is increased, simply because of increase in the number of type-II inclusions. The same trend is observed for the other two systems of potassium hydrogen phthalate and succinic acid (Fig. 2b and c).

The water ratio of the agglomerates was lower than that of the less agglomerated crystals in the corresponding size range for all the systems examined. This suggests that agglomerates are not always more impure compared to less agglomerated crystals. The purity of agglomerates can be higher. It depends on the suspension conditions. High purity of agglomerates is suggested to due to the high purity of primary crystals of small size. The small size of primary particles plays a key role for producing agglomerates of high purity.

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