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Liquid inclusions in crystals produced in suspension crystallization

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Abstract

Sodium chloride, potassium chloride, succinic acid and potassium hydrogen phthalate crystals were crystallized batchwise in an agitation vessel and the total volume of liquid inclusions per crystal, V (μm^3), was measured as a function of crystal size, d (μm). The found data of the total volume, including literature data from a continuous crystallizer, was correlated with a simple equation, $V=4.0\times10^{-6}d^4$. Most of the inclusions observed in sodium chloride and potassium chloride crystals were layer inclusions, which were aligned two-dimensionally in parallel with crystal faces. This type of inclusion pattern was suggested, with the help of the results of additional in situ experiments under a microscope, to be caused by the adhesions of small crystals to growing crystals and mechanical contacts imposed to these crystals during growth. Although the layer pattern was not found in the other crystals examined, the same mechanism was considered to work for the inclusion formation. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Suspension crystallization; Crystal purity; Liquid inclusion; Sodium chloride; Potassium chloride

1. Introduction

Purity is one of the important requirements for commercial crystals. Purity drop is caused mainly by mother liquids included in crystals during crystallization. For seeking for a better technique producing pure crystals, it is important to clarify the mechanism for inclusion formation in industrial crystallization.

Some important results can be found in literature on the formation of liquid inclusions. Garside and Larson [1] found a mechanism for mother liquid inclusion formation in their in situ observation experiments of secondary nucleation. Liquid inclusions were formed on contacts of a rod with a potash alum crystal under a microscope. Inclusions were found just at a contact site (direct contact-induced formation). On the other hand, Shimizu and Kubota [2] reported that liquid inclusions were formed not only at a contact site but also at other positions of the surface of a potash alum crystal (non-direct contact-induced formation). The same results as those of Shimizu and Kubota [2] were reported by Saito et al. [3] for a sodium chloride crystal. Saito et al. [3] discussed the non-direct contact-induced mechanism in detail. Another type of inclusion formation, caused by the adhesion of a small crystal, was reported by Toyokura et al. [4]. Mother liquid was trapped in spaces between an attached small crystal and the large seed crystal (direct adhesion-induced formation). However, for inclusion formation caused by the adhesion of a small crystal, Saito et al. [5] reported a different mechanism (non-direct adhesion-induced formation). Liquid inclusions are formed at other positions apart from the adhesion point. Shimaoka et al. [6] reported the formation of liquid inclusions caused by the presence of small crystals. Many liquid inclusions were observed in the seed crystals at the parts grown after the addition of small crystals. However, no mechanism of liquid inclusion formation was proposed in the paper [6].

In all the investigations described above, ‘ideal’ experimental techniques were employed. Observations of liquid inclusion formation in an actual suspension crystallizer has not been reported. Mechanisms applied for an actual suspension crystallizer have not been clarified yet.

The purpose of this study is to propose a mechanism for the formation of liquid inclusions in crystals growing in suspension in an agitated vessel. The total volume and the location of liquid inclusions formed in crystals were examined. Further, in situ observation experiments under an optical microscope were conducted to simulate typical phenomena (mechanical impacts and the adhesion of small crystals) occurring on growing crystals in an industrial crystallizer.

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2. Experimental

2.1. Crystallization experiments

The total volume of inclusions per crystal was measured for sodium chloride, potassium chloride, succinic acid and potassium hydrogen phthalate crystals produced in batch agitation crystallization. A relation between the volume of inclusions and the crystal size were investigated.

2.1.1. Experiments on sodium chloride

An aqueous solution of sodium chloride (saturation temperature=333 K) was kept unsaturated for a few hours at 338 K in an agitated vessel (flask) of 2 l. The solution was quickly cooled down to 293 K with agitation (250 rpm). On cooling spontaneous crystallization occurred immediately. In 2 h from the start of cooling, crystals were separated from the final slurry by filtration. The final suspension density was 0.004 (–) in volume ratio.

Liquid inclusions in a sodium chloride crystal had irregular shape originally but they changed to cubic shapes as they were or after splitting (see Fig. 1) depending on the size by heating in an oven at 323 K for 24 h. But the location of inclusions did not change. After treated in the oven, crystals were classified by sieving. About 15–120 crystals from each size class were selected randomly, depending on the number of crystals in each size class. Volumes of all liquid inclusions in the selected crystals were determined by measuring the side length of cubic inclusions. This measurement technique is troublesome but it has an advantage that the location of each liquid inclusion can be identified simultaneously.

Table 1
Crystallization condition

	Potassium chloride	Succinic acid	Potassium hydrogen phthalate
Crystallization time (h)	0.25	0.32	0.47
Stirring rate (rpm)	250	250	250
Saturated temperature (K)	343	338	298
Starting temperature (K)	346	342	299
Terminal temperature (K)	293	293	284
Final suspension density	0.038	0.15	0.0050

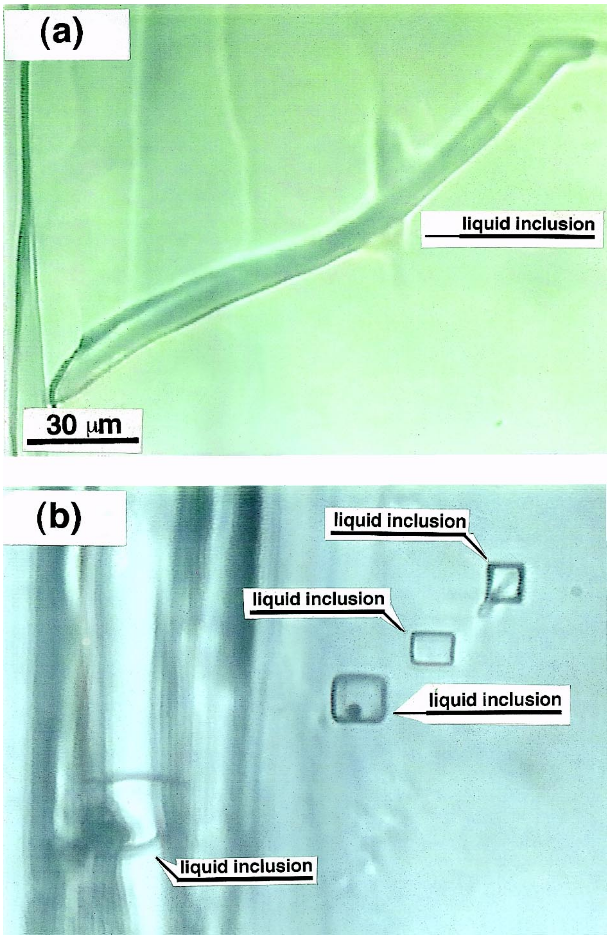

Fig. 1. Change in inclusion shape by heating: (a) irregular shape of inclusion just after formation; (b) split regular shape inclusions (24 h heating at 323 K).

For comparison, non-agitation crystallization experiments were also performed for sodium chloride.

2.1.2. Experiments on other materials

Potassium chloride, succinic acid and potassium hydrogen phthalate (KAP: $C_6H_4COOHCOOK$), were crystallized by cooling under agitation in the similar way as in the experiments on sodium chloride crystals. Experimental conditions are shown in Table 1.

In the case of these crystals, the weight of water in crystals was measured with a Karl–Fischer aquameter after the crystal had been dried in the oven for several days in order to remove liquid adhered on the crystal surface. The total weight of water per crystal was converted to the total volume of liquid inclusions per crystal. The conversion was made using solubility and density data in literature by assuming that the volume was filled with solution saturated at a room temperature (293 K).

2.1.3. Crystal size

The crystal size d is defined as the cube root of the volume of a crystal. Crystals were classified into appropriate size groups by sieving. In the case of sodium chloride and potassium chloride crystals the average size d was approximated by the arithmetic mean of the successive sieve openings, because the crystal shape is cubic. On the other hand, as succinic acid and potassium hydrogen phthalate crystals are not cubic, the volume of a crystal is calculated from the average weight, which was obtained from the weight of many (200–2000) crystals in each size class.

2.2. In situ observation experiments — sodium chloride

The following two in situ experiments were performed to simulate typical phenomena associated with the crystal-

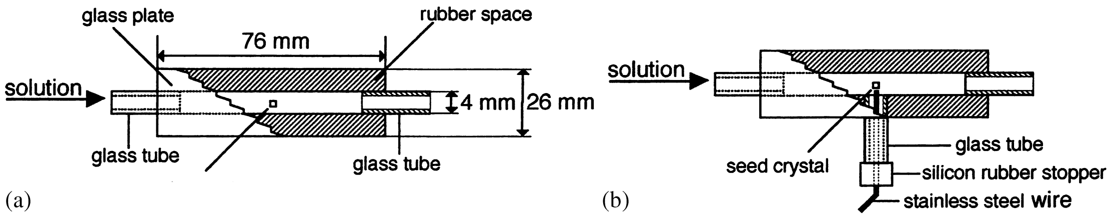

Fig. 2. Flow cells for (a) adhesion experiments and (b) contact experiments, and observation spot on the seed crystal for the both experiments.

lization process in an actual industrial suspension crystallizer. As typical phenomena occurring in the crystallizer, adhesion of small crystals to large growing crystals and mechanical impacts imposed to these large crystals were simulated as follows for a single sodium chloride seed crystal.

2.2.1. Adhesion experiments

Experimental apparatus and technique are almost the same as those of a previous work [7]. Sodium chloride solution (saturation temperature=313 K) was fed to a flow cell (Fig. 2a), on the bottom of which a seed crystal (0.5–3 mm in size) was fixed. The cell was placed on the stage of an optical microscope. At first, a seed crystal was grown in a clear solution (with no small crystals) at 308 K. Then it was made to grow in the presence of small crystals of micrometer level, by changing the route of solution flow, on the way of which small crystals were generated in a nucleator by agitation. The surface of the seed crystal was scanned by a microscope continuously with a low magnification (2×) to search if a small crystal has been attached by any chance. Just at the moment when a small crystal was found adhering onto the surface of the seed crystal, the flow was switched back again to the clear solution to avoid a further adhesion of other small crystals. The surface and inside of the seed crystal were observed with a higher magnification (40×).

2.2.2. Contact experiments

The same apparatus as that in the above mentioned ‘adhesion experiment’ was used with a minor modification to the flow cell. A glass tube was attached to the cell (Fig. 2b). A metal rod (stainless steel wire of 400 μm in diameter) was inserted through the attached tube and the top end of the rod was set close to the seed crystal. A mechanical impact, which was made by manipulating the rod, was repeated a few to about 20 times in each experiment. The seed crystal was observed continuously before and after the mechanical impacts with a microscope (40×) to check inclusion formation. The solution temperature, supersaturation and the size of a seed crystal were the same as those of the adhesion experiments.

3. Results and discussion

3.1. Total volume of liquid inclusions per crystal

3.1.1. Sodium chloride — agitation crystallization

The total volume of inclusions per crystal, V (μm^3), is plotted as a function of crystal size, d (μm), in Fig. 3 (●). It was correlated with crystal size as

$$V = 4.0 \times 10^{-6} d^4 \qquad (1)$$

Fig. 3a and b show typical examples of inside horizontal cross-sectional view of crystals. No liquid inclusions are seen in a 60 μm crystal (Fig. 4a). As observed here, most of small crystals of this size level did not have inclusions. In only a few crystals inclusions were formed. On the other hand, inclusions can be seen in a 170 μm crystal (Fig. 4b). These liquid inclusions are aligned in parallel with the side faces of the crystal in this figure. They were observed two-dimensionally as vertical layers (layer inclu-

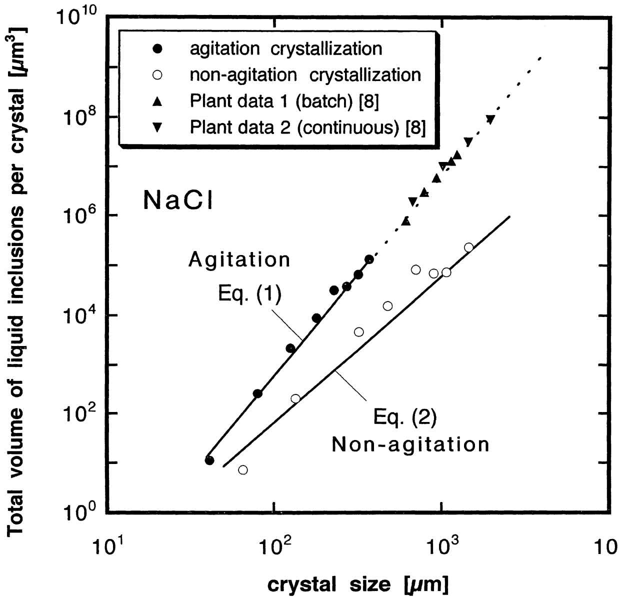

Fig. 3. The total volume of liquid inclusions per crystal as a function of crystal size for sodium chloride crystal.

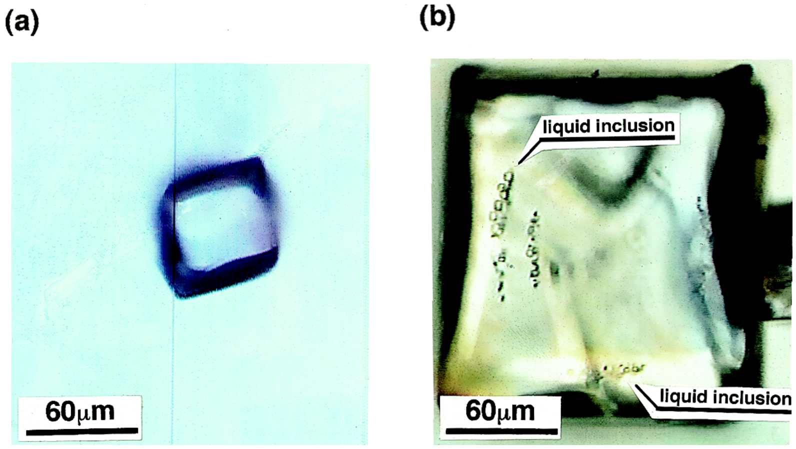

Fig. 4. Inside cross-sectional pictures of sodium chloride crystals obtained from agitation crystallization.

sions) schematically shown in Fig. 5. In this figure only vertical layers of inclusions are shown for simplicity, but horizontal inclusion layers were also formed. The same location pattern of inclusions could be seen in other crystals larger than about 70 μm.

There are two types of inclusion-free regions (Fig. 5) as shown with open circles on a horizontal cross-sectional plane. One is located in the central part of a crystal and the other is near a vertical edge of the crystal. (Note: these regions are three-dimensional actually.) In the rest of these regions many layer inclusions can be seen.

The fact that layer inclusions appeared periodically in the inclusion-existing region as shown in Fig. 4b is an important finding. It suggests that some important thing triggering formation of liquid inclusions happened periodically during crystal growth in suspension. A mechanism for the periodic formation of layer inclusions was proposed later after discussing the results of in situ observation experiments.

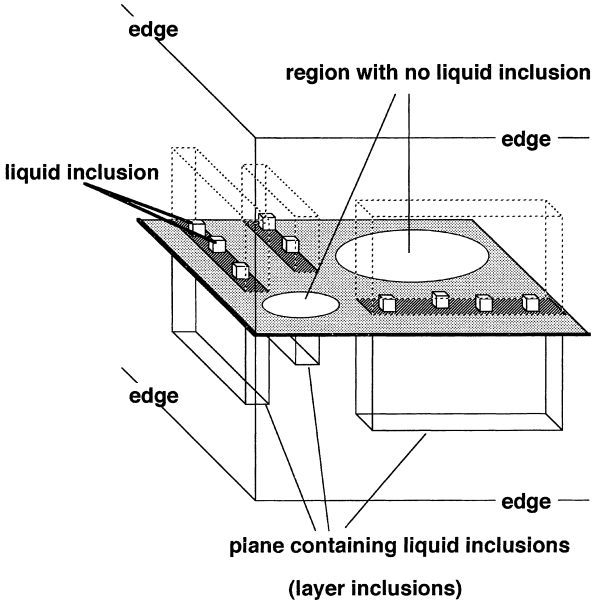

Fig. 5. Schematic arrangement of liquid inclusions inside a sodium chloride crystal.

In Fig. 3, literature data of the total volume of inclusions measured on sodium chloride crystals from an Krystal–Oslo type crystallizer by Ehara et al. [8] are also shown. Data 1 are from the batch system (▲) and Data 2 from the continuous system (▼). The crystallization conditions (temperature, suspension density, supersaturation, agitation speed and so on) were much different from ours of laboratory scale. However, these plant data could be plotted on a dashed line, which was extrapolated from our laboratory data (solid line). Thus, the total volume of liquid inclusions per crystal was able to be correlated with a single equation with the crystal size regardless of crystallization condition. It is interesting and would be useful for estimation of the amounts of inclusions or the impurity level of crystals.

3.1.2. Other materials — agitation crystallization

In Fig. 6 the total volume of inclusions measured for the other crystals (potassium chloride (□), succinic acid (△), potassium hydrogen phthalate (▽)), together with literature data [9] for ammonium perchlorate crystal (◇), are overplotted on the sodium chloride data. The volume of liquid inclusions per crystal for these compounds was found to lie on the line obtained for sodium chloride (Eq. (1)). The Eq. (1) can be applied approximately to all the compounds examined. This is surprising. Some general mechanisms is suggested to work for inclusion formation in suspension crystallization.

3.1.3. Sodium chloride — non-agitation crystallization

The total volume of liquid inclusions for non-agitation crystallization is also plotted in Fig. 3 (○) as a function of crystal size. The total volume of inclusions is small in the case of non-agitation. The agitation effect is clearly seen.

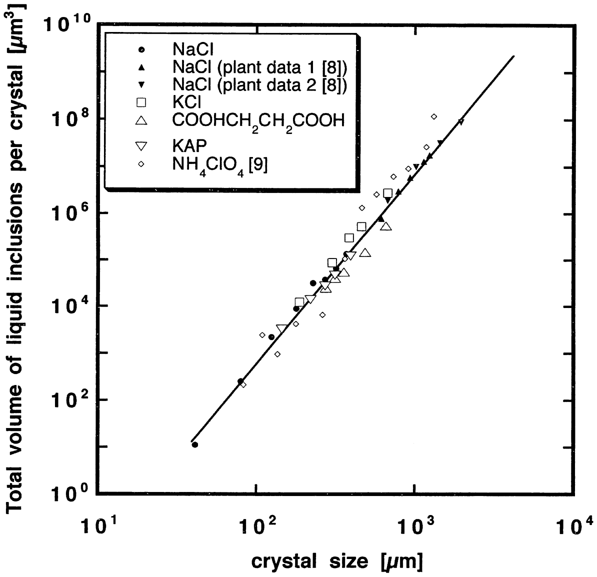

Fig. 6. The total volume of liquid inclusions as a function of crystal size (data for all the materials examined and literature data).

The volume was correlated by

$$V = 9.1 \times 10^{-5} d^3 \tag{2}$$

The exponent 3 of the equation suggests that liquid inclusions are distributed uniformly in a crystal. However, the liquid inclusions were observed to be aligned in parallel with surfaces of crystals as same as those for agitation crystallization. But the population density of inclusions was much lower than that of agitation crystallization experiments. Gentle attachments of small crystals, which is considered to occur with low probability during growth, would be cause for inclusion formation in this case.

3.2. *In situ observation of liquid inclusion formation*

3.2.1. *Inclusion formation caused by adhesion of a small crystal*

Fig. 7 is an inside cross-sectional picture of a seed crystal after growth. The seed crystal was grown in the clear solution at first and then it was grown in the suspension of small crystals. The front surface advances by growth to the left in the figure. A small crystal (about 10 μm) adhered onto the front surface by chance when the front surface was just at the point B. The adhered small crystal had been buried already into the seed crystal when the picture was taken. (It cannot be identified in the picture.) However, in the region C after the adhesion, many liquid inclusions are observed as dark bands (layer inclusions), which were developed two-dimensionally in parallel with the front surface of the seed crystal. A similar observation was reported by the present authors previously [3]. These layer inclusions are non-direct adhesion-induced inclusions, because they are formed apart from the adhesion site. This layer inclusion is the same as inclusions observed in crystals produced in agitation crystallization (Fig. 4b). Layer inclusions observed in crystals produced in a suspension crystallization is suggested to be generated by the successive adhesions of small crystals.

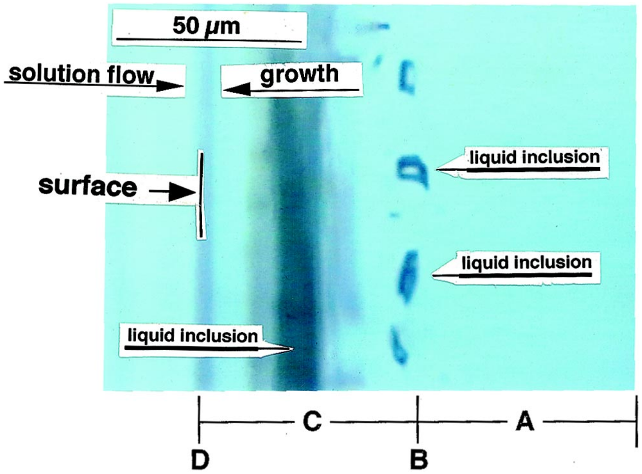

Fig. 7. Inside cross-sectional picture of a crystal after the adhesion of a small crystal (in situ simulation experiment).

3.2.2. *Inclusion formation caused by contacts*

Fig. 8 shows an inside cross-sectional picture of the seed crystal, to which mechanical contacts were made just at the time when the front surface of the crystal had passed the point B. There are no liquid inclusions before the contacts (region A). However, dark bands consisting of many liquid inclusions (layer inclusions) are observed at left hand side of the point B. These liquid inclusions were formed at different part apart from the site the mechanical contacts were made. Therefore, this type of inclusion formation can be named the

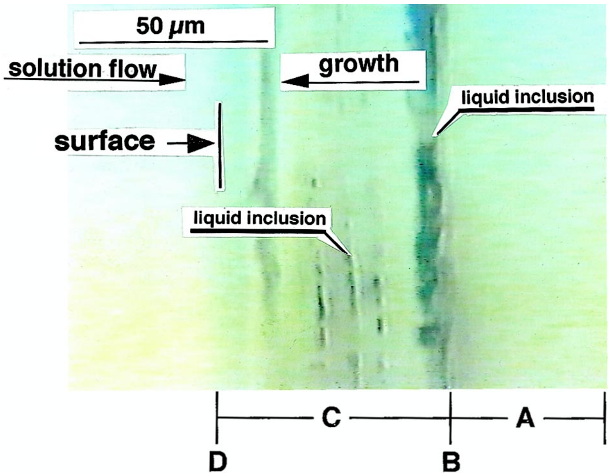

Fig. 8. Inside cross-sectional picture of a crystal after contacts (in situ simulation experiment).

non-direct contact-induced mechanism. Similar observations were reported previously by the authors [5].

3.2.3. Mechanism of layer inclusion formation and probability of the occurrence

In a previous study, the adhesion experiment and the contact experiment were carried out many times [5,10]. Layer inclusions, as shown in Figs. 7 and 8, can be concluded to be generated not only on the impacted surface or the adhered surface but also on the other surfaces. Some structural defects were believed [3,5] to be generated somewhere on the crystal surfaces by the adhesion or the mechanical contacts. From these defects new micro-steps originate successively followed by the development of macro-steps by bunching. Although these micro-steps can not be seen, only macro-steps could be observed. Faster active macro-steps were frequently observed to overlap the preceding macro-steps which proceed slowly. At this moment of overlapping mother liquid was observed to be trapped under the overlapping step. Thus, many liquid inclusions were trapped two-dimensionally in parallel with crystal surfaces.

Further, we must add another important experimental fact that every adhesion or contact did not always bring formation of layer inclusions. As reported previously, layer inclusions were observed 17 times of 81 adhesion experiments (21%) [10] and 13 times of 54 contact experiments (24%) [5].

3.3. A proposed mechanism for liquid inclusion formation in suspension crystallization

Inclusions in sodium chloride crystals produced in the batchwise agitation crystallization were mostly layer inclusions, which are seen periodically in crystals in parallel with crystal surfaces, as shown typically in Fig. 4b. This type of inclusions were also observed in potassium chloride crystals. The isolated inclusions, which are considered to be caused by the direct mechanisms, were relatively few. Therefore, the inclusions in suspension crystallization could be caused mainly by the non-direct (adhesion and contacts)-induced mechanisms. The fact that layers appeared periodically can be explained by the fact that the adhesions of small crystals and the contacts are not always effective, but they work with a low probability, as mentioned above.

It is interesting that the total volume of inclusions per crystal can be correlated with a single equation, regardless of the material. This suggests a general mechanism working on the formation of liquid inclusions. The non-direct mechanism could be a possible mechanism. The exponent 4 of Eq. (1), which means the probability of inclusion formation increases with an increase in crystal size, could be explained qualitatively by the increasing probability of attachment of small crystals and the contacts imposed to the growing large crystals encountered. Agitation speed should be another important factor affecting the frequency of the attachments and contacts. However, it had no effect on the liquid inclusion formations (see Eq. (1)). This is probably because change in the probability of the attachment and the contacts is not so large under the condition of ordinary suspension crystallization.

Incidentally, completely developed layer inclusions in succinic acid crystals and potassium hydrogen phthalate crystals, were not found but ‘line’ inclusions were found. Both of these crystals, which were plate-like, were not considered to be thick enough for the formation of layer inclusions. However, the same non-direct mechanisms are suggested to work for these crystals, too.

4. Conclusions

1. Layer inclusions were found in crystals (sodium chloride and potassium chloride) produced in batch agitation crystallization. These inclusions appeared periodically in parallel with the crystal faces. By the way, line (not layer) inclusions were found in the thin plate-like (succinic and potassium hydrogen phthalate) crystals examined.
2. The total volume of inclusions per crystal was correlated with Eq. (1) for sodium chloride crystals produced in this study. Literature data including those from continuous and batch actual crystallizers and the measured data for other (potassium chloride, succinic acid and potassium hydrogen phthalate) crystals were all correlated by Eq. (1). This suggested a general mechanism working to form liquid inclusions.
3. The layer inclusion patterns observed in crystals obtained in agitation crystallization was the same as those found in a single crystal in the in situ simulation experiments. This suggests that the non-direct adhesion and contact-induced mechanisms play a major role in liquid inclusion formation in agitation crystallization.

References

[1] J. Garside, M.A. Larson, Direct observation of secondary nuclei production J. Cryst. Growth 43 (1978) 694.
[2] K. Shimizu, N. Kubota, In situ observation of the surface of barium nitrate crystals growing in supersaturated solution Kagaku Kogaku Ronbunshu 12 (1986) 388.
[3] N. Saito, M. Yokota, A. Sato, N. Kubota, Formation of liquid inclusion in a single sodium chloride seed crystal triggered by adhesion of small crystals and its mechanism Kagaku Kogaku Ronbunshu 24 (1998) 486.
[4] K. Toyokura, H. Sakai, R. Uchida, Effect of suspended fines on crystal growth, in: Proceedings of the 10th Symposium on Industrial Crystallization, Bechyne, Czechoslovakia, 1989, p. 215.
[5] N. Saito, A. Sato, N. Kubota, Growth enhancement and liquid inclusion formation by contacts on NaCl crystal AIChE J. 45 (1999) 1153.
[6] T. Shimaoka, H. Takiyama, M. Matsuoka, Growth rate enhancement of sodium chloride crystals by newly-born mycrocrystals in supersaturated solutions Kagakukogaku Symp. Ser. 49 (1995) 58.

[7] M. Yokota, N. Saito, J. Hirai, A. Sato, N. Kubota, Crystal growth rate enhancement caused by adhesion of small crystals AIChE J. 43 (1997) 3264.

[8] L. Ehara, S. Kowaki, M. Sasaki, A. Otsubo, A study on the cavity ratio NaCl crystals made by Oslo type crystallizer Bull. Soc. Sea Water Sci. Jpn. 50 (1996) 77.

[9] N. Hiquily, C. Lagurie, Inclusion formation in the ammonium perchlorate crystal — influence of surfactans, in: Proceedings of the 9th Symposium on Industrial Crystallization, Hague, The Netherlands, 1984, p. 79.

[10] N. Saito, M. Yokota, A. Sato, N. Kubota, Liquid inclusions in a growing sodium chloride crystal caused by adhesion of fine crystals, in: Proceedings of the International Symposium on Industrial Crystallization, Tianjin, China, 1998 p. 365.