Growth Enhancement and Liquid-Inclusion Formation by Contacts on NaCl Crystal

Saito Noboru, Yokota Masaaki, Sato Akira, and Kubota Noriaki
Dept. of Applied Chemistry and Molecular Science, Iwate University 4-3-5 Ueda, Morioka 020-8551, Japan

A large number of crystals grow continuously and simultaneously in an industrial suspension crystallizer. These crystals collide with each other, an impeller, and the crystallizer wall. During these frequent mechanical impacts, crystals produce secondary nuclei or break into fragments. Further, crystals agglomerate or stick to each other upon impact. Therefore, crystals in suspension are not said to ‘‘grow’’ only by a molecular-level growth mechanism like that assumed in the BCF theory or the two-dimensional nucleation growth theory. A brief summary of these theories is given in a recent book (Söhnel and Garside, 1993).

Interesting experiments were performed to simulate the phenomenon of small crystals sticking to larger ones in an industrial suspension crystallizer (Yokota et al., 1997). Yokota et al. observed the growth behavior of a single sodium chloride crystal fixed in a flow cell under a microscope. The growth rate was shown to be enhanced temporally for a few minutes after a micrometer-level small crystal was attached. This growth-rate enhancement was accompanied by temporal step generations, which were thought to originate from invisible cracks induced by mechanical stress caused by the mismatched lattice orientation of an attached small crystal. This type of growth-rate enhancement was also confirmed by Saito et al. (1998). In the latter article, another interesting experimental result—that liquid inclusions are formed on a small-crystal attachment—is also reported. Liquid-inclusion formation is undesirable in industrial crystallization, since it may reduce the degree of purity and quality (or degree of crystallinity) of the product crystals.

Using an optical microscope, Garside and Larson (1978) and Garside et al. (1979) observed secondary nucleation induced by a mechanical contact made on a potash alum seed crystal. They observed that liquid inclusions were formed only around a contact site during growth after the contact. Unfortunately, they did not discuss this observation in detail, probably because their main interest was not liquid inclusion formation but secondary nucleation.

In this article, we report the effects of mechanical contacts on the growth behavior of a single seed crystal of sodium chloride. Growth-rate enhancement and liquid-inclusion formation were observed. These experiments were made to simulate the actual collisions that frequently occur in an industrial suspension crystallizer.

Experimental Studies

In situ observations of sodium chloride crystal growth were carried out by using an apparatus similar to that in an earlier article (Yokota et al., 1997). A minor modification was made to a flow cell (Figure 1) so that a metal rod (stainless wire, 400 μm in diameter) was inserted through a tube close to a seed crystal mounted on the bottom of the flow cell. The cell was fixed on a microscope slide. Sodium chloride solution saturated at 313 K was fed through a heat exchanger into the flow cell by a metering pump, where the temperature of the solution was lowered to 308 K (supercooling of 5 K). The face growth rate of the front surface of a seed crystal was

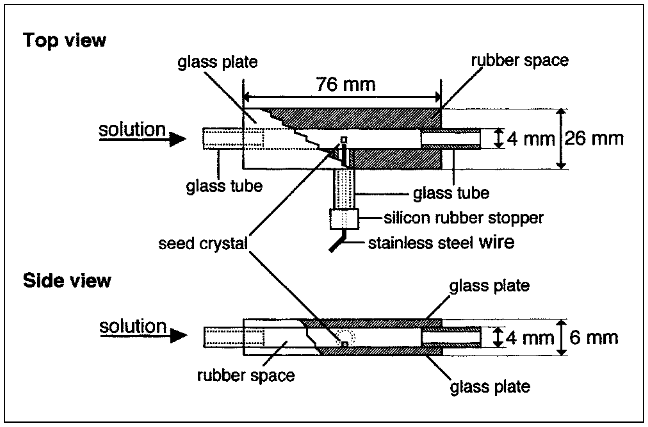


Figure 1. Flow cell with a stainless-steel rod for contact.

Correspondence concerning this article should be addressed to S. Noboru.

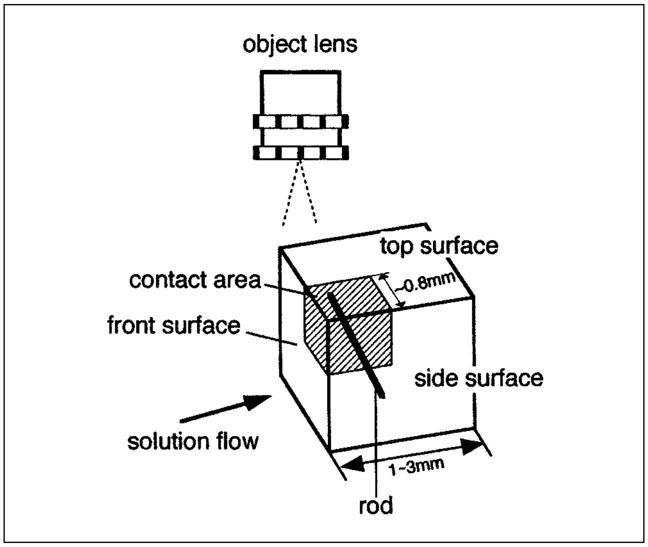


Figure 2. Observation spot and contact area on the seed crystal of sodium chloride.

measured and the topographic structure of the top surface was observed (Figure 2). The inside cross section of the crystal was also scanned by lowering the focal point of the microscope to a horizontal plane inside the crystal.

Contacts were made manually by manipulating the stainless-steel rod. Because of this, the contacts could not be made at a predetermined position on the seed crystal, but were made at a point somewhere within a distance of about 0.8 mm from the corner where top, front, and side corners intersect (see the shaded zone in Figure 2). Contacts were repeated a few to 20 times for each experiment. These repetitions were not able to be made precisely at the same position, but the contact position varied within an area of about 0.5×0.5 mm. The seed crystal was prepared by recrystallization, and its size ranged between 1 and 3 mm.

Results and Discussion

Growth-rate enhancement and liquid-inclusion formation by mechanical contacts

Typical time variation in the growth rate of the front surface of a sodium chloride crystal is shown in Figure 3a. The growth rate was constant before contact began after 147 min (see the arrow in the figure). Thus, the crystal grew at a stable rate under the ideal condition of no contacts. However, the crystal growth rate increased suddenly just after the contacts started; these were made on the top surface and on an edge between the top and front surfaces. The growth rate remained at a high level for a few minutes, and then it decreased gradually. Similar growth behavior was observed for the case of the attachment of a small crystal (Yokota et al., 1997).

An inside horizontal cross-sectional view of the crystal is shown in Figure 3b. The position C in the figure indicates the location of the front surface at 199 minutes, which corresponds to the point b in Figure 3a. The front surface grew from A to C in Figure 3b. There were no liquid inclusions in the region before the contacts (from A to "contacts" in Figure 3b). But many liquid inclusions were seen as layers to the left in the region after the contacts. The layers were seen to spread in parallel with the front surface throughout the vertical cross section of the crystal, although the contacts were made on a very limited part on the top surface and the edge of the crystal.

Topographic change leading to liquid-inclusion formation

Figure 4 shows a sequence of topographic pictures of the top (not front) surface of the same seed crystal in the same time period seen in Figure 3. The surface before the contacts (Figure 4a) was smooth, with no visible growth step. It was still very smooth just after the contacts (Figure 4b), because the picture was taken at a point just after contact. But at about 1.5 minutes after the contacts, macrosteps began to be generated successively near the edge at which the front and top surfaces intersect, and moved progressively in the direc-

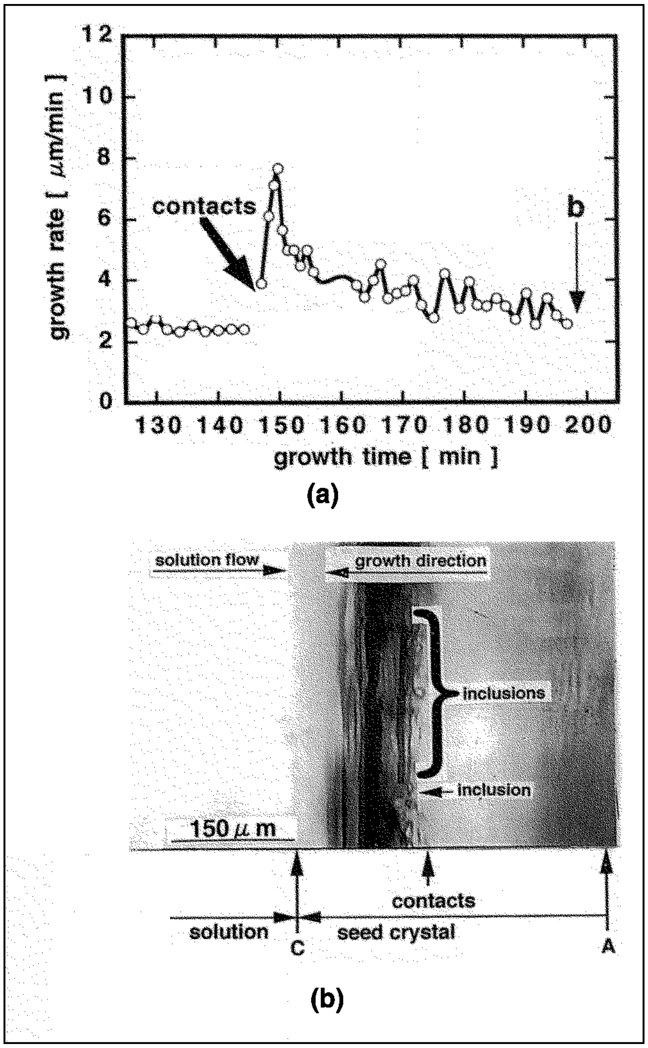
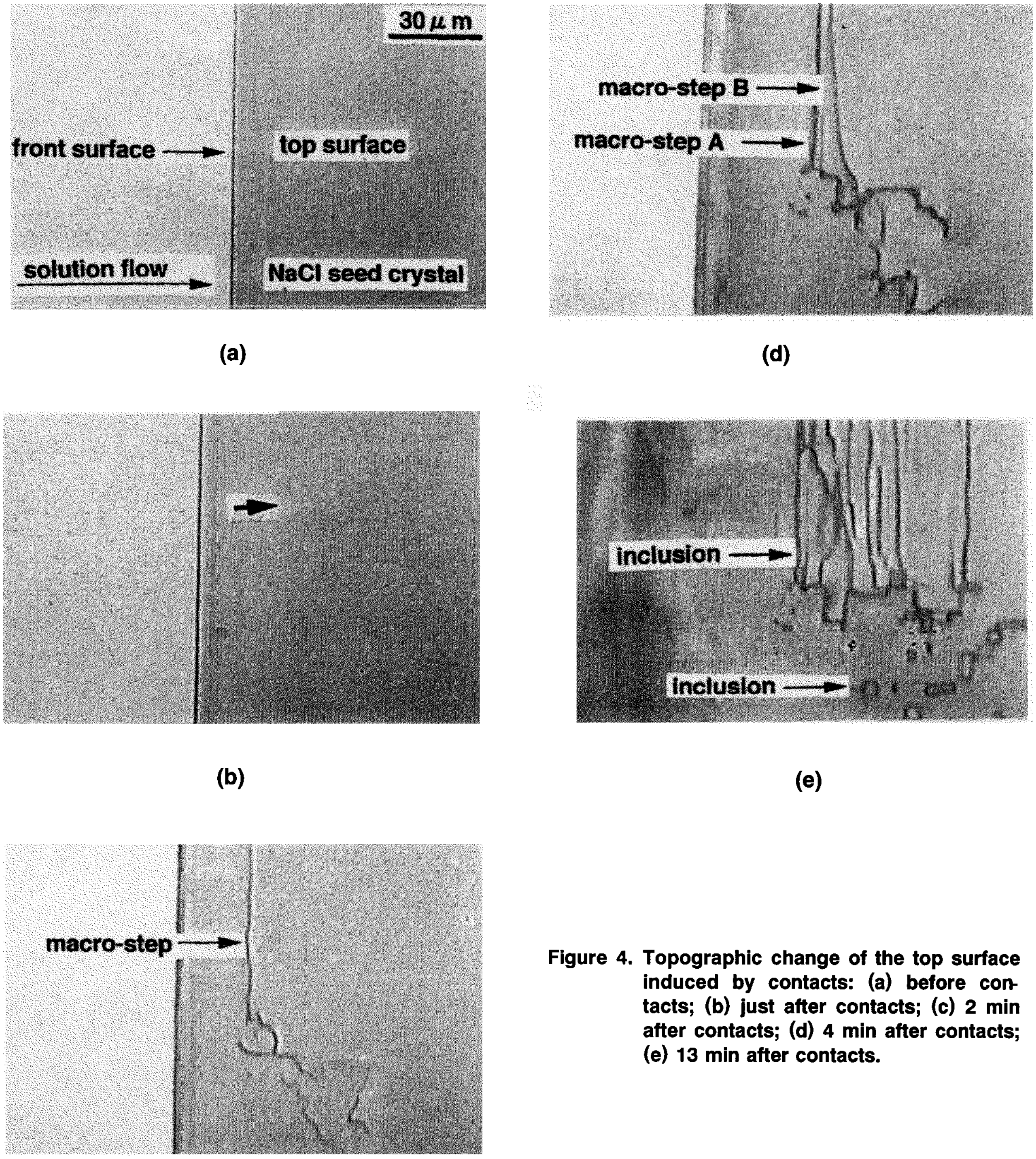


Figure 3. (a) Typical example of time variation of growth rate; (b) inside cross section of the seed crystal at time of *b* in part (a).

Contacts indicate the location of the front surface at time of the contacts.



(a) (d)

(b) (e)

(c)

Figure 4. Topographic change of the top surface induced by contacts: (a) before contacts; (b) just after contacts; (c) 2 min after contacts; (d) 4 min after contacts; (e) 13 min after contacts.

tion indicated by the arrow in Figure 4b. The macrosteps became large during moving by bunching, and were then seen clearly (Figure 4c). This period of active step generation and movement corresponded to the period of growth enhancement in Figure 3a. The same topographic change was seen to occur on the front surface, at which growth rate was measured. It was confirmed by scanning the top surface that macrosteps did not propagate from the contact site.

Figure 4d is a snapshot of the top surface of the crystal just at the moment when a new macrostep B is passing over an old stationary macrostep A. After its passage, mother liquids were trapped under the subsequent step and incorporated into the crystal as liquid inclusions. Liquid inclusions were generated one after another until the creation of macrosteps ceased, and then the surface became smooth again. Inclusions remained in the crystal as shown in Figure 4e. Many inclusions were formed, until they finally became one horizontal layer. The vertical layer seen in Figure 3b was thought to have formed in the same manner. This type of inclusion formation is different from that of Garside and Larson (1978) and Garside et al. (1979). Their inclusions were formed only in a small region around the contact site. It must be noted that inclusions similar to those of Garside and Larson (1978) and Garside et al. (1979) were also formed in our experiments, but they did not become a layer as just mentioned.

Probability of liquid-inclusion formation

It is interesting to know how frequently inclusion formation and growth-rate enhancement can be induced by the mechanical contacts. We repeated the same experiments 54 times using different seed crystals, where only the vertical inclusion layer was checked and the growth rate of the front surface was measured. In 23 trials (42.6%) no growth enhancement and no inclusion formation were observed. Growth-rate enhancement occurred in the other 31 trials (57.4%), however, and inclusions were observed (13 trials) in 41.9% of the 31 trials. Inclusion formation was always accompanied by growth-rate enhancement. It should be noted that growth-rate enhancement is not a sufficient condition, though it is a necessary one.

The degree of growth-rate enhancement, which is defined as the ratio of an instantaneous maximum growth rate recorded after contacts to the average growth rate before the contacts, $G_{\max}/G_0$, differed widely, as shown in Figure 5. Distribution is shown in Figure 5a, for the case where no inclusions were formed, while Figure 5b shows distribution for the case where inclusions were formed. These data do not contain inclusion formation for just the contact site. Inclusion formation of this type (Garside-Larson type) was observed in most of the seed crystals examined, regardless of growth-rate enhancement.

Mechanical contacts are expected to be made on a crystal growing in an industrial suspension crystallizer much more frequently than were made in this experiment. Growth enhancement must therefore occur frequently and many liquid inclusions must be formed. In fact, many inclusions were observed in the commercial sodium chloride crystals we examined. Further, any type of commercial crystal from a suspension crystallizer is thought to contain liquid inclusions, because the mechanism for inclusion formation is not specific to the sodium chloride crystal. According to Wilcox (1968), liquid inclusions were found in many inorganic crystals ($AgNO_3$, KCl, K_2SO_4, LiCl, $Na_2S_2O_3 \cdot 5H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Ba(NO_3)_2$, KIO_3, KI, $KBrO_3$ and $KClO_3$) as well as in organic crystals (potassium biphthalate, urea, naphthalene, benzonic acid, oxalic acid, thiourea, and hexamethylenetetramine). It is also expected that growth-rate enhancement will occur for a variety of crystals growing in suspension in industrial crystallizers.

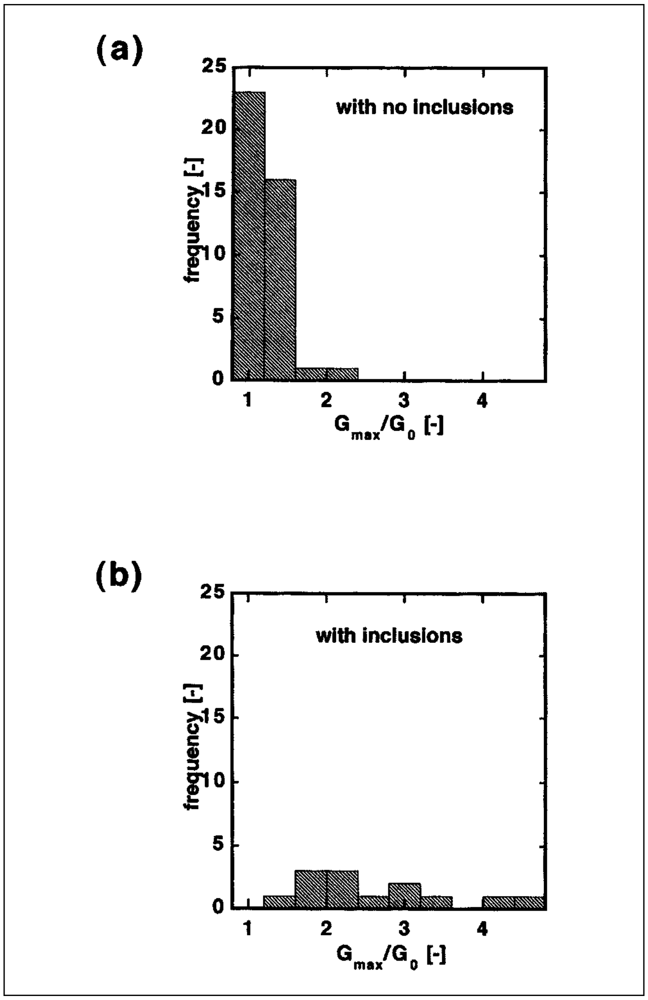


Figure 5. Distribution of growth-rate enhancement degree: (a) with no inclusion; (b) with inclusion.

Acknowledgment

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