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Specially Grown Salt Crystals for Carrying Additives

Susan Halász[1] and Tasuku Nakai[2]

[1]*Research Institute for Technical Chemistry of the Hungarian Academy of Sciences, Veszprém, Hungary*
[2]*Hiroshima Institute of Technology, Hiroshima, Japan*

ABSTRACT

A new approach has been developed to utilize the non-stationary growth forms of NaCl for producing porous salt crystals which can take up valuable additives either by adsorption or by entrapping them as inclusions. Two different types of these carrier crystals are introduced here: first the microporous crystals (size 100–200 μ) are discussed which have perfectly formed nucleus in their centre covered by holed layers of irregular growth. The other type is represented by 5–10 mm dendritic crystals with 30–40% free inner volume or 5–30% inclusions and fast dissolving ability. These specially grown salt compositions can distribute, store, save and release the additives according to their carrier-additives ratio and micro-structure.

INTRODUCTION

Growth of almost completely packed high quality crystals is a well known demand in modern technology, but to grow irregular crystals which contain growth defects such as inner pores or caves is quite unusual.

When we refer to the utilization of growth instabilities, we mean the formation of a rather regular pattern of discontinuities within the structure of the crystal which can take up sensitive or etheric bioactive additives finely distributed, or can be carriers of small dosed nutrients. Traditional crystallization practice considered the formation of macro defects to be undesirable because of the risk of impurity entrapping and the significant consequential changes in the physical and chemical properties of the crystals.

A knowledge of modern crystallization allows more flexibility in the operation due to its more precise methods for controlling the kinetic processes.

The main objective of this paper is to show that the study of the micro-world of crystals can still be the source of new technological approaches. Chernov (1989) has stated..."The shape of the growing crystal serves as the simplest indicator of the atomic growth mechanism."

THEORETICAL

Crystals which grow from pure solution at low supersaturation are generally well developed and their shape is related to unit cell structures. The mode of incorporation of molecules or ions into the lattice determines the morphological stability or instability of the face. The NaCl type alkali halogenide crystals can exhibit their stationary growth at very low supersaturation (Hartmann, 1978):

$$\Delta\mu << \Gamma/L \qquad (1)$$

where $\Delta\mu$ is the chemical potential difference; Γ is the system property parameter including the volume of the building ions, surface tension, etc.; and L is the size of the crystal. $\Delta\mu$ can be expressed by the supersaturation ratio, S:

$$\Delta\mu = kT \ln S \qquad (2)$$

where k is the Boltzmann constant and T is the absolute temperature.

If the condition (1) cannot be fulfilled, instead of regularly grown surface layers, dendritic, skeletal or even filamentary shapes may appear revealing the existence of growth instabilities. The theoretical analysis of the interface instability was made by Brice and Bruton (1974). They considered a flat surface of a growing crystal in its supersaturated solution. The growth occurs by a random two-dimensional nucleation followed by lateral spread, see Fig. 1.

Two kinds of growth are distinguished: the rate of expansion of the nucleus filling up the plane, marked with f*:

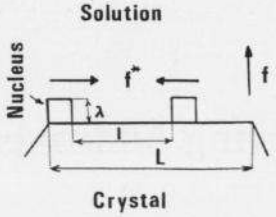

Fig. 1. A growth face (Brice and Bruton, 1974). f, Linear growth velocity normal to crystal face (cm s^{-1}); f*, nuclei spreading velocity (cm s^{-1}); L, crystal face dimension (cm); l, distance between nuclei (cm); λ, height of nucleus (cm).

$$f^* = (D/\lambda)\,(\Delta c/c) \tag{3}$$

where D is the diffusion coefficient ($cm^2\ s^{-1}$); λ is the height of the nucleus (cm); and $\Delta c/c = \sigma$ is the relative supersaturation ($\sigma = S - 1$).

The normal growth of the face, f is given as:

$$f = \lambda/\tau \tag{4}$$

where τ is the time between nuclei being formed one on the top of another. One step can start either by two-dimensional nucleation or by dislocations.

If a new nucleus forms before the existing nuclei reaches the edges, the face becomes unstable. The face is stable if the distance l between nuclei or between the nucleus and the edge is less than the size L of the face. The critical size over which the instable growth may start can be determined as:

$$L < f^* \lambda/f \tag{5}$$

Slaminko and Myerson (1981) employed the above stability criterion (5) to determine the critical size of sodium chloride and predicted its critical dimension as 5×10^{-5} m, over which the formation of inclusions, i.e. liquid entrapping within macro defects, could be expected. However the experimental verification was not in tune with the calculation. The first detailed work on the formation of inclusions was published by Denbig and White (1966). Depending on the desupersaturation velocity during the batch crystallization of hexamethylene tetramine, they observed the following stages: over a certain size open cavities appeared and then, when the relative supersaturation fell below $\sigma = 0.03$, the caves "healed" just entrapping liquid.

Mullin (1985) surveying the problem has concluded that impurities may be formed in a variety of ways: fast and interrupted growth; sudden change in local conditions; adsorption of impurities; temperature or concentration gradients in the crystallizer, etc. According to Chernov's interpretation (1989), temperature or concentration fluctuations may cause the decomposition of smooth layers and their transformation into rough surfaces. While the kinks — the most favourable position for a particle to enter the crystal lattice — do not exceed 10^{-2}–10^{-6}% of the whole of the atomic sites on a flat surface, they can occupy tens of percents of all the sites of a rough one. This can explain why rough surfaces may grow so quickly and can lead to the formation of macro defects.

EXPERIMENTAL

Material and techniques

An aqueous solution of technical grade sodium chloride saturated at room temperature was used for the investigations carried out either in static evaporation pan or precipitated by diluted ethanol in a laboratory scale (1 l volume) three-phase column. The composition of the raw material was determined by an ARL 3410 type ICP-DES spectrometer and the following impurities were found: S = 0.26%, K = 0.17%, Ca = 0.33% and Mg = 0.022%.

The observation of the outer and inner structure (taking segments) of the product crystals was made by an JSM-50A scanning electron microscope (SEM) in the Central Laboratory of Veszprém University. According to the applied Specimen Coating Method (Glauert, 1977) the sample was fixed to a holder and coated with 15–20 nm thick gold in a Balzers-type sputtering device and the surface was then photographed by SEM. The measuring conditions were: 25 kV accelerating voltage, 10^{-12} Å probe current secondary electron image.

RESULTS AND DISCUSSION

Formation of inclusions in micro crystals

NaCl crystals have the tendency to grow smooth external faces although their inner structure can be quite poor as is shown in Fig. 2. The question was: whether micro crystals could develop inclusions? To answer the question, laboratory scale investigations were carried out in a flexible three-phase bubble column crystallizer, semi-batch way. The precipitant alcohol was pre-vaporized into the bubble producing air stream. Because the precipitant was uniformly dispersed into the solution, a precise control of supersaturation was exercised over the whole batch process. The experimental set up is shown in Fig. 3.

Spontaneous nucleation and a controlled growth within $\sigma = 0.3$–0.05 supersaturation range were allowed according to a desupersaturation program, given in Fig. 4.

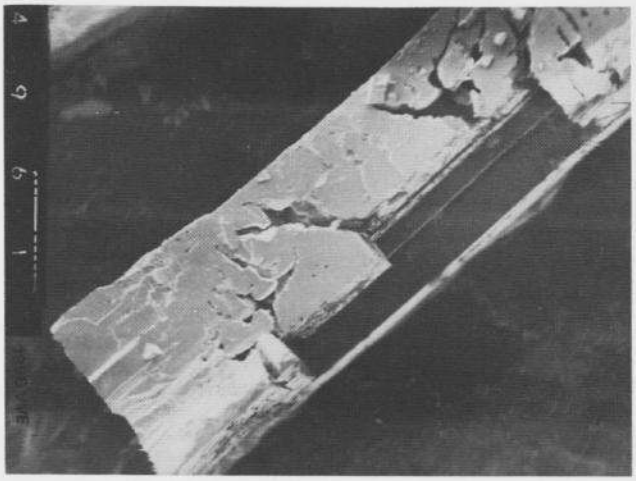

Fig. 2. Large inclusion with a 2 mm long salt crystal (segment).

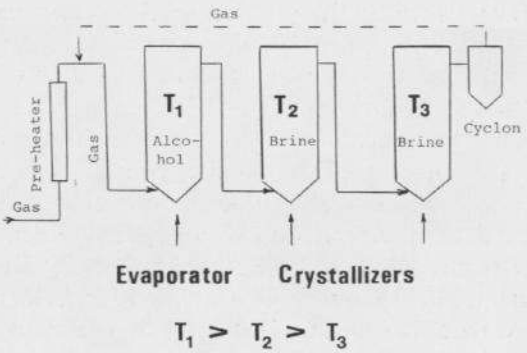

Fig. 3. Experimental set up for brine precipitation. (T_1, T_2, T_3, working temperatures).

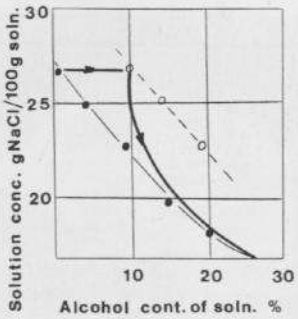

Fig. 4. Concentration diagram of the brine–ethanol system. (—•—, solubility; —o—, supersolubility; →—, desupersaturation).

In consequence of the special mixing conditions and temperature-concentration gradient within the crystallizer, growth instabilities could develop. Instead of smooth layers, a pattern of macro defects manifesting as a set of open pores were found on each crystal surface (Fig. 5).

After carefully peeling of the surface layers of the crystal, a perfectly grown seed (nucleus) of size 50–60 μ became visible (Fig. 6.).

The observed critical size is in very good agreement with the theoretically predicted 5×10^{-5} m value (Slaminko and Myerson, 1981). Considering the mechanism of inclusion formation (Denbig and White, 1966) it was found possible to produce microcavities unsealed. In other words: because of the precise supersaturation control we could avoid the final stage of inclusion formation, i.e. the entrapping of impurities, although we could not omit the danger of secondary nucleation, as is shown in Fig. 7.

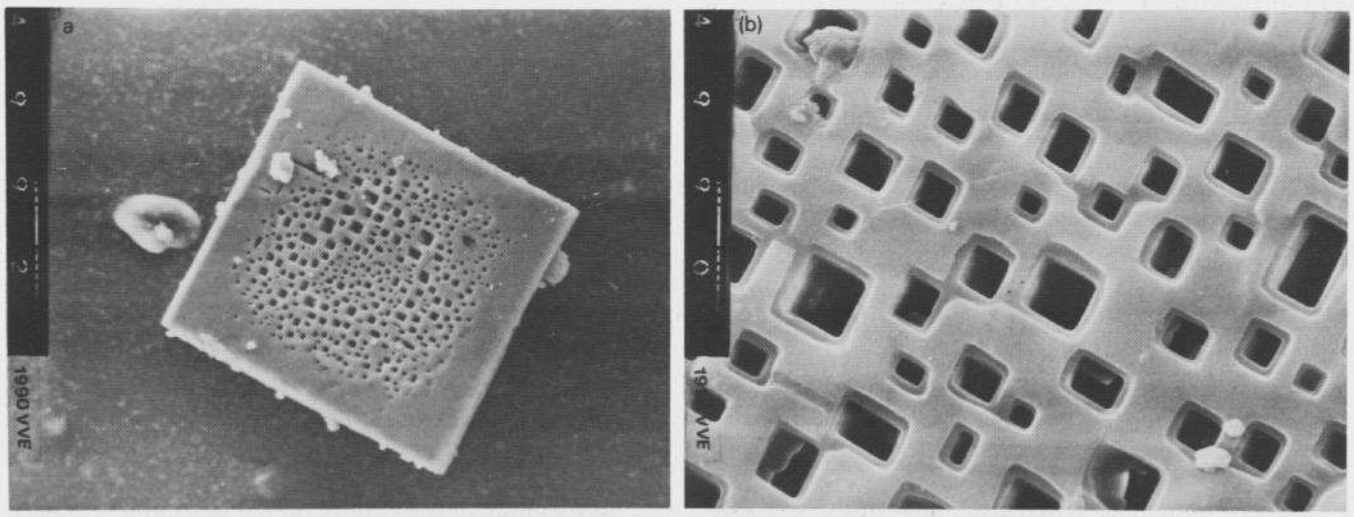

Fig. 5. The face of an irregularly grown NaCl crystal at different magnifications. (a) Magnification 350 ×, 1 cm = 28 microns. (b) Magnification 3000 ×, 1 cm = 3.3 microns.

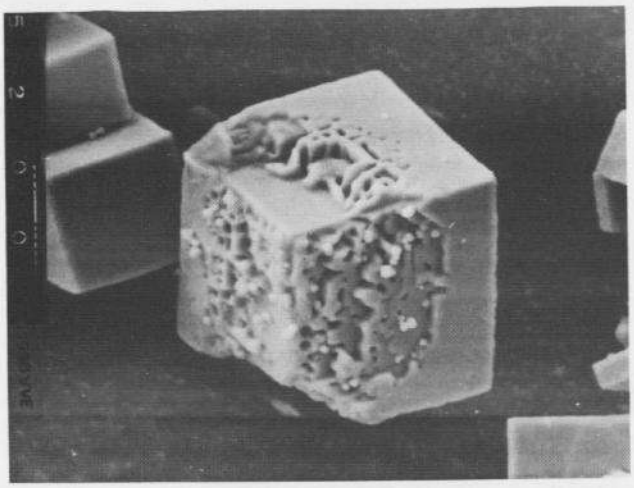

Fig. 6. The inner structure of the irregularly grown salt (magnification 300 ×, 1 cm = 33 microns).

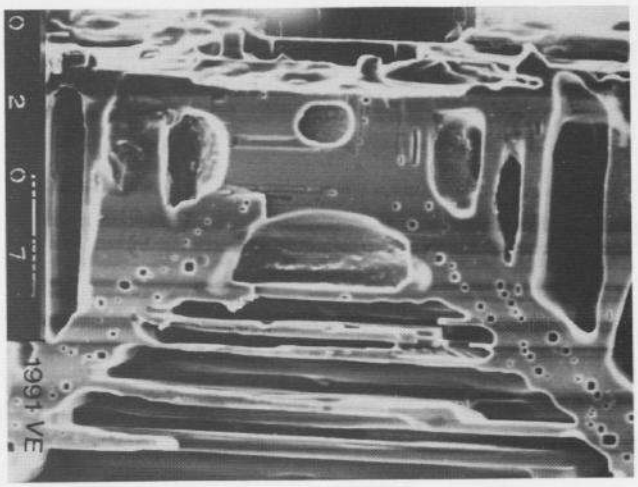

Fig. 8. The inner centre of the dendrite (magnification 150 ×, 1 cm = 66 microns).

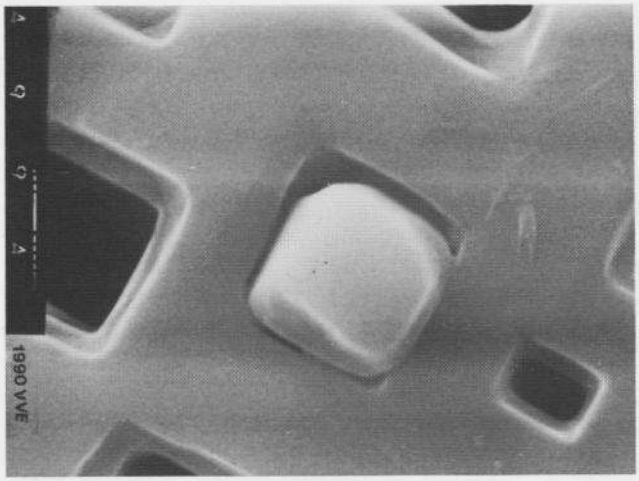

Fig. 7. A secondary nucleus born in the pore (magnification 10,000 ×, 1 cm = 1 micron).

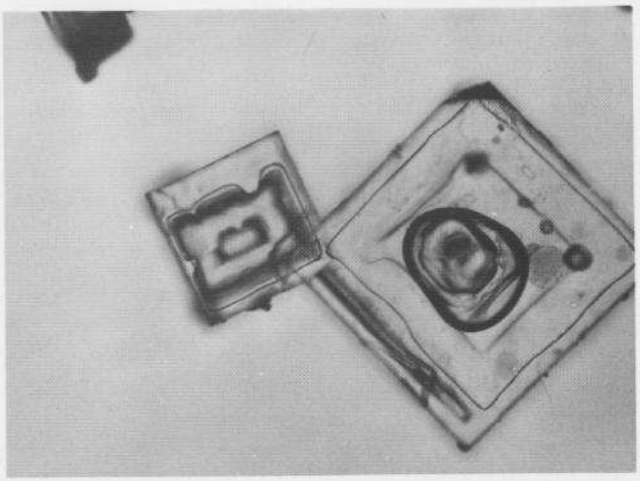

Fig. 9. Liquid inclusions in dendrites (magnification 38 ×, 1 cm = 260 microns).

Dendritic crystals for carrying additives

Dendrites of sodium chloride grow "starving", i.e. the transport of fresh supersaturated solution is retarded either by the lack of agitation in the static evaporation system or by the blocking effect of certain impurities. Both effects were utilized in our case.

After cutting off the top of such a large (10–15 mm) dendrite, large empty cavities were found inside the crystal arranged concentrically around the centre following the main growth directions (Fig. 8.).

These dendrites have about 30–40% free inner cavities. Their density is about 1.6 g/cm^3. These crystals can take up liquid phase additives in the form of inclusions as shown by the following example. Brine with potassium iodide additive (0.03% KI in the solution) was crystallized in the above-described way. The product crystals entrapped a considerable amount of liquid inclusions as Fig. 9 clearly demonstrates.

When a mother crystal is opened its liquid inclusion crystallized at once, but with quite a different habit from that shown in Fig. 9. The typical hopper shape clearly indicates the presence of accumulated potassium iodide in this solidified inclusion (see Fig. 10.).

In extreme cases the inclusion can occupy about 50 volume percent of the carrier. Figure 11 shows open and covered crystals of NaCl a few millimetres in size. These crystals can carry and save a consider-

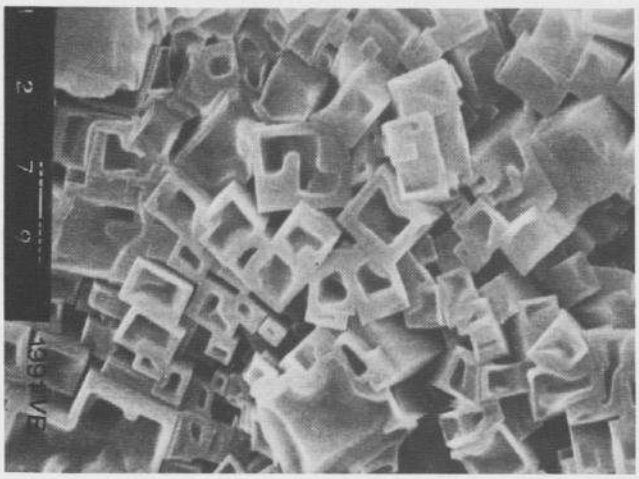

Fig. 10. Solidified inclusion with KI impurity (magnification 300 ×, 1 cm = 33 microns).

Fig. 11. Open and covered boxes of NaCl (magnification 3 ×, 1 cm = 3 mm).

able amount of inclusions, for example, bioactive etheric oils as shown in Fig. 12.

CONCLUSIONS

According to traditional crystallization, crystal defects caused by growth instabilities are regarded as undesirable because of the risk of impurity entrapping. By studying the micro-structure of irregularly grown NaCl crystals, we have concluded that macro defects can be utilized for carrying valuable additives. A strict control on the formation of defects is needed in order to avoid the uptake of undesirable impurities. Two types of carriers have been introduced:

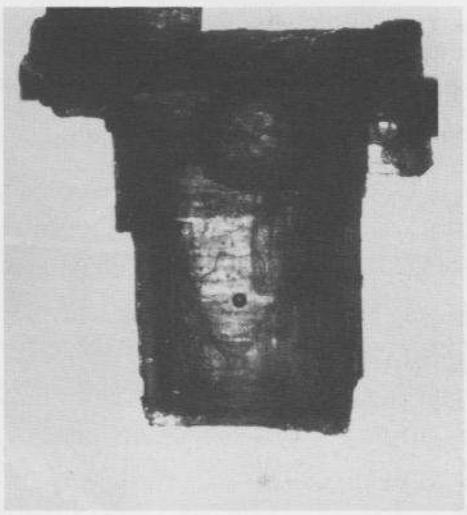

Fig. 12. A composition of inorganic carrier and organic inclusion (magnification 30 ×, 1 cm = 300 microns).

– microcrystals of size 100–200 μ, with perfectly grown 50 μ centres and porous external layers with a concentric pattern of 1–3 μ open pores;

– dendritic crystals a few millimetres in size with large (even 50 volume percent) inner cavities (open and covered state).

The specially grown crystal compositions can distribute, store, save or release the additives according to the carrier–additive ratio and microstructure or can be the carriers of small dosed nutrients. The formation mechanism of macro defects in NaCl crystals was found to be the result of interface instabilities developed under certain non-stationary growth conditions, as follows: in the case of fast precipitation when the relative supersaturation exceeded the value of $\sigma = 0.3$ the growth occurred by nucleation and was then followed by the composition of deformed layers deposited on the nucleus.

The size of the nucleus, and hence the critical size over which the formation of macro defects started, was found to be 50–60 μ corresponding with the predicted critical size according to the Brice and Bruton theory.

Maintaining the supersaturation above $\sigma = 0.05$, the last stage of inclusion formation, i.e. the healing process of macro defects and impurity trapping, was omitted.

In other cases of utilizations, valuable additives were trapped within the carrier salt.

REFERENCES

Brice, J.C. and Bruton, T.M., 1974. The stability of facets on growing crystals. J. Crystal Growth, 26: 59–60.