CHAPTER - IV

EFFECT OF GEL PARAMETERS ON NUCLEATION AND GROWTH OF $CaSO_3$ CRYSTALS IN SILICA GEL

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4.1 Introduction

The gel growth of single crystals is one of the important methods and it is being widely used and investigated by several laboratories in view of the growing interest in the field of crystal growth [1-6]. Already a variety of single crystals suitable for solid state experimentation have been grown in silica gel [7-11]. The gel method has unique characteristic of suppression of nucleation centres; the aqueous solutions of the reactants produce microcrystallization because of the fast chemical reaction. The gel technique is, in fact, the only method of growing crystals when the materials decompose at temperatures below their melting points and also for those not having suitable solvents for crystallization.

The gel medium prevents turbulence and remains chemically inert. It provides a three-dimensional structure which permits the reactants to diffuse at a desirable controlled rate. The gel supports the growing crystal and at the same time helps to grow crystal without exerting major forces upon it. The softness and the uniform nature of forces which it exerts upon the growing crystals results in the growth of good quality single crystals.

Though the ionic diffusion and velocity are slowed down by the soft three-dimensional gel framework, yet this suppressed reaction rate is much more than the one required for limited nucleation. Hence studies on nucleation control in gels are primary and most important factors to grow single crystals useful to solid state technology. Therefore, the present study has been undertaken with a view to control the nucleation density and increase the size of the crystals by varying various gel parameters.

So far there are no published data available regarding the nucleation studies on $CaSO_3$ on the growth of single crystals of $CaSO_3$, Patil and Rao [12] have recently reported the successful growth of these crystals in silica gels. The present chapter gives the results of the detailed studies made on nucleation and growth of these crystals as a function of gel parameters such as gel density, gel pH, concentration of feed solutions, gel ageing, intermediate neutral gel column and concentration programming.

4.2 Experimental Procedures

Crystal growth experiments were carried out in one end open corning glass tubes of length 20 cm and inner diameter 2.5 cm. The chemicals used were: Loba "G.R." $CaCl_2$, Na_2SO_3 and B.D.H."Anala R" acetic and hydrochloric acids.

The following chemical reaction was employed for the growth:

$$CaCl_2 + Na_2SO_3 \longrightarrow CaSO_3 + 2\ NaCl$$

The gel solutions were prepared by mixing pure sodium silicate solution with the required amount of 1N acetic acid. For each 25 c.c. of gel solution 10 c.c. 1M $CaCl_2$ was added. After the gels were set, the feed solution of Na_2SO_3 was carefully placed above the set gels for crystallization. Double distilled water was used throughout the study. Completion of crystallization (with crystal size upto 10 x 5 x 4 mm^3) took about 2 months. The results were based on the statistical average of six sets of experiments.

4.3 Observations and Discussion

4.3.1 Effect of Density of Gels:

The gels of various densities were obtained by mixing sodium silicate of specific gravity 1.01 to 1.06 to 1N acetic acid by keeping the pH constant at 5 by adding the required quantity of concentrated hydrochloric acid drop by drop using a pipette. It is observed that the transparency of the gel decreases as the gel density increases. Also, the gels with higher densities set earlier than the gels with lower densities. It is clearly seen from the Figures 1(a)-1(c) that an increase in gel density increased the contamination of the crystals with silica gel and thereby affected their quality and shape. It may be noted that well defined and transparent single crystals were obtained with sodium silicate of specific gravities below 1.03. On the other hand, gels of below 1.03 specific gravity took very long time (more than a month) to set and are mechanically not very strong. A specific gravity of 1.02 g/cm^3 has been found to be the lower practical limit. It is clear from Figure 2 that an increase of gel density decreases the nucleation density which is due to the fact that greater gel density results in smaller pore size which is in agreement with the observations made by Henisch [13].

4.3.2 Effect of pH of Gels:

The pH values of gels were varied from 2 to 11 by adding a few drops of concentrated hydrochloric acid (for acidic gels) and ammonium hydroxide (for basic gels) before setting of the acetic acid gel solutions. It is observed that as the pH of the gel increases, the transparency of the gel decreases. Also, the gel with pH values greater than 7 is not homogeneous. The crystals growing at higher pH values ($\approx$ 8) are not transparent and well defined. This is due to the contamination of crystals with silica gel, because of the pH increases the box-like network structure of the gel changes to a loosely bound platelet structure which lacks cross-linkages; the cellular nature becomes less distinct [13]. It is clearly seen from the Figures 3(a)-3(c) that as pH of the gel increases, the number of crystals decreases, and at very high pH values ($\approx$9) the crystals are not well defined. Figure 4 shows that the total number of crystals decreases with increase in the pH value which may be due to the improper formation of cells at higher pH values of gels.

4.3.3 Effect of Concentration of Feed Solution:

The dependence of concentration of feed solution was investigated by preparing gels of same density (specific gravity, 1.03) and same pH ($\approx$ 5). After setting the gels, feed solutions of Na_2SO_3 of various concentrations ranging from 0.1M to 1.5M were added carefully. Figure 5 shows crystals growing in gels at three different concentrations of feed solutions. The variation of number of crystals with concentration of feed solution is shown in Figure 6. This indicates that as the concentration of feed solution increases the nucleation density increases which is due to the increased availability of sulfite ions.

4.3.4 Effect of Ageing of Gels:

To study the effect of gel ageing, gels of same pH ($\approx$ 5) and density (sp. gr. 1.03) were prepared. The gels were allowed to age for different periods before adding the feed solution. Feed solution of Na_2SO_3 of concentration 0.5M was added over the gels. Crystals growing in gels of three different ages are shown in Figure 7. Figure 8 shows the variation of number of crystals versus gel ageing. It is clear from these figures that as the ageing of the gel increases the number of crystals decreases. One possible explanation of ageing might be that there is a progressive formation of cross-linkages between the siloxane chains, which results in gradual diminishing cell size. This will lead to a lowering of the nucleation density, since many nuclei, whether homogeneous or heterogeneous, will find themselves in cells of too small size to support visible growth. The increased number of the cross-linkages reduce the rate of diffusion of ions through the gel. Because of smaller nucleation number, the gel ageing increases the size of the crystals slightly without any change in the quality.

4.3.5 Effect of Intermediate Neutral Gel:

The effect of the intermediate neutral gel on the number of crystals and their size was studied by adding different amounts of acetic acid neutral gels (i.e., gels without $CaCl_2$ or Na_2SO_3) over the $CaCl_2$ incorporated gels. Here gels of 1.02 specific gravity were used. Since the gels are very dilute the boundary between $CaCl_2$ incorporated gel and the neutral gel is not seen. The neutral gels were allowed to set and the feed solution was then added. Figure 9(a)-9(c) shows the crystals growing in tubes with three different heights of intermediate neutral gel columns. A graph of number of crystals versus the length of the intermediate neutral gel column is shown in Fig. 10. The intermediate neutral gel will slow down the reaction between the reactants, and reducing the number of critical nuclei. The intermediate neutral gel increases the size of the crystals considerably without affecting their quality.

4.3.6 Effect of Concentration Programming:

To study the influence of concentration programming, feed solution of Na_2SO_3 concentration 0.05M was placed over the $CaCl_2$ incorporated acetic acid set gels. Then, the concentration of the feed solution was increased at the rate of 0.02M per day by removing 20c.c. of the above feed solution and replacing it by an equal amount of higher concentration feed solution. The process was continued till the concentration Na_2SO_3 reached upto around 0.5M when nucleation started and resulted in a few nucleation centres. Still further increase of concentration upto 1.5M resulted in the growth of the already formed nuclei. Figures 11(a) and 11(b) show crystals growing without and with concentration programming respectively. In the case of concentration programming, as the concentration of the diffusant increases, the already formed nuclei act as sinks and the resulting establishment of radical diffusion patterns reduces concentrations and appears thus to inhibit the formation of additional nuclei. Subsequent increases of feed solution concentration lead to faster growth instead of formation of new nucleation. The existing crystals are thus able to grow non-competitively and their quality is correspondingly better as shown in Figure 11(b). It has been found empirically that frequent small steps are more beneficial than a few large concentration increases. The method has yielded crystals of larger size and a higher degree of perfection than those produced without programming. The size increased by a factor of 5.

4.4 Conclusion

Transparent single crystals of $CaSO_3$ can be obtained at low pH values (below 6) with low density of gels (below 1.03 specific gravity of sodium silicate). Gel ageing and intermediate neutral gel column reduce the nucleation centres and increase the size of the crystals without affecting their quality. The nucleation density increases with the increase of concentration of feed solution. By concentration programming, the size of the crystals can be increased.

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