CHAPTER 4

EFFECT OF GEL PARAMETERS ON NUCLEATION AND GROWTH OF $KClO_4$ SINGLE CRYSTALS

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4.1 INTRODUCTION

The problem of nucleation is of great importance in practical operations, since the crystals which grow in any particular gel system compete with one another for solute. This competition limits their size and perfection, and it is obviously desirable to suppress nucleation until, ideally, only one crystal grows in a predetermined location. The available techniques have not yet reached this level of perfection.

In gel growth, nucleaion controll can be achieved to some extent by changing a variety of gel parameter viz., concentration of feed solutions, gel density, gel pH, Intermediate neutral gel column and concentration programing. Studies on the effect of concentration of feed solutions on nucleation and growth of lead sulphide, alkaline earth orthophosphate, rare earth double sulphate have already been reported [1-3]. Transparent single crystals of calcite have been obtained between pH value of 7 and 9 [4]. Blank et al. [5,6]

Show that nucleation can be controlled using intermediate neutral gels. Nucleation control, for various crystals, by concentration programming has been studied by several workers. [8-10]. The successful growth of $KClO_4$ crystals using various crystallization apparatus has been described in the previous chapter [chapter-3]. The present chapter describes the studies on the effect of gel parameters on nucleation and growth of $KClO_4$ crystals.

4.2 EXPERIMENTAL PROCEDURES

The silica gel [acidified sodium silicate] was used as the growth media throughout this study. the gel was prepared by mixing pure sodium silicate solution with the required amount of 1 N perchloric acid. The variation of pH with the amount of 1N perchloric acid for different specific gravities of sodium silicate solution were taken. The gel solutions thus prepared were then transferred to 2.5 cm diameter and 30 cm length test tubes and allowed to set at a constant temperature of 22°C. After the gels were set, the feed solution of KNo_3 was placed above the gels for crystallization. Analytical reagent grade chemical and doubly distilled water were used throughout this study. Completion of crystallization (with crystal size upto 4 X 6 X $8mm^3$) took about 15 to 20 days. The results are based on the statistical average of five sets of experiments.

4.3 OBSERVATIONS AND DISCUSSION

4.3.1 EFFECT OF CONCENTRATION OF FEED SOLUTION

To study the effect of concentration of feed solution, gels of same pH and density were prepared. Feed solutions of different concentrations varying from 0.4 to 1.8N were added over the set gels. Fig. 4.1 shows crystals growing at three different concentrations of feed solutions. The variation of nucleation density with concentration of feed solution is shows by graph in Fig. 4.2. This indicates that at higher concentration of feed solutions, because of the enhanced availability of potassium ions, the nucleation density increases.

4.3.2 EFFECT OF AGING OF GELS

To investigate the effect of gel aging, gels were allowed to age for various periods before adding the feed solution. Crystals growing in gels allowed to age for three different periods are shown in Fig 4.3. Fig. 4.4 is plot of age of gels verses the nucleation density. As reported by Henisch [9], gel aging reduces the cell size and consequently the rate of diffusion of ions into the gel. The gel aging has not pronounced effect on the size or the quality of the crystals.

4.3.3 EFFECT OF GEL DENSITY

The gels of different densities were obtained by mixing sodium silicate of Sp.gr. 1.02 to 1.06 to 1N perchloric acid keeping pH constant at 5 by adding a few drop of CH_3CooH. It is observed that the transparency of the gel increases as the gel density decreases. It is seen from Fig. 4.5 (a) - 4.5 (c) that, an increase in gel density increases the contamination of the crystals with silica gel and there by 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 1.04. It is clear from Fig. 4.6 that an increase of gel density decrease the nucleation density which is due to the fact that greater gel density results in smaller pore size as demonstrated first by Henisch[9].

4.3.4 EFFECT OF pH OF GELS

The pH values of gels were varied from 2 to 10 by adding a few drops of acetic acid before setting of the perchloric acid gel solutions. It is observed that, as the pH increases the transparency of gel decreases. It is evident from Fig. 4.7 that the crystals growing at higher pH values are not transparent and well defined this is due to the contamination of crystals with silica gel, because as the pH increases the box-like network structure

of the gel change to a loosely bound platelet structure which lacks cross-linkages; the cellular nature becomes less distinct[9]. Fig. 4.8 shows that the nucleation density decrease with increases in the pH value which may be due to the improper formation of cells at higher pH values of gels.

4.3.5 EFFECT OF INTERMEDIATE NEUTRAL GEL

To study the effect of the height of the intermediate neutral gel column, different amounts of acetic acid set gel solution were added over the perchloric acid set gels. The neutral gels were also allowed to set and the feed solution was then added. Fig. 4.9 shows that the crystals growing in tubes with different heights of intermediate neutral gel column•A graph of nucleation density versus the length of the intermediate neutral gel column is shown in Fig. 4.1. The intermediate neutral gel will slow down the rate of diffusion of KNo_3 thus slowing down the reaction between the reactants, the reducing the number of nuclei. The intermediate neutral gel does not have remarkable effect on size or quality of the crystals.

4.3.6 NUCLEATION CONTROL BY CONCENTRATION PROGRAMMING

Over the perchloric acid set gel, 30ml of 0.2N KNo_3 solution was placed the strength of this feed solution was increased at the rate of 0.01N per day by removing 20ml

of the above feed solution and replacing it by an equal amount of higher concentrated feed solution the process was continued till the concentration of KNo_3 reached upto around 2.5N when nucleation started and resulted in a few nucleation centres. Fig. 4.11 (a) and 4.11 (b) show crystals growing without and with concentration programming respectively. It is considered that with very dilute reactants, the amount of material diffused through the gel is attained under these circumstances, a few nuclei are formed on increasing the concentration, further growth of the existing nuclei is preferred to the formation of additional ones. Crystals grown by this method are transparent and larger than those grown without this method.

4.4 CONCLUSIONS

Transparent single crystals of $Kclo_4$ can be obtained at low pH values (below 6) with low density of gels [below 1.04 sp.gr. of sodium silicate]. Gel column reduce the nucleation centres without affecting the quality of the crystals grown. The nucleation density increases with the concentration of the feed solution. By concentration programming, the size of the crystals can be increased and their number decreased.

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