

# The Kinetics of Crystallization of Scale-Forming Minerals

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## ABSTRACT

*Reviewed here is the kinetics of crystal growth of sparingly soluble minerals such as calcium carbonate, calcium sulfate, and barium sulfate, which frequently cause scaling problems in oil fields. For all three electrolytes, the crystal growth is surface controlled and follows a second-order rate law with an activation energy for the growth process of 10 to 20 kcal mol<sup>-1</sup>. The growth of calcium sulfate seeded crystal above 100°C demonstrates the importance of characterizing polymorphic transformation processes. Phosphonate scale inhibitors show differing modes of inhibition in systems precipitating CaCO<sub>3</sub> and CaSO<sub>4</sub>.*

## INTRODUCTION

The formation of crystals of scale-forming, sparingly soluble minerals continues to be a very serious problem for the petroleum engineer. Scaling arises from a specific set of geological, physical, and chemical conditions. Geological factors such as ground water circulation and mineral composition may mediate in scale formation as may physical factors such as pumping rate, well pressure, and the extent of fluid addition to the oil-bearing formation. However, the principal factors regulating scale formation in the oil field are chemical and such investigations can answer many of the problems. For example, scale caused by the addition of surface water to an oil-bearing formation can often be eliminated by chemical treatment of the injected water. A more important scaling arises from changes in subsurface mineral solubility due to variations in temperature and pressure under down-hole conditions. The difficulties are compounded by the fact that conditions frequently encountered under down-hole conditions, notably high pressure and high temperature, cannot be readily simulated in the laboratory. Sampling of an aqueous solution brought to the surface for analysis can lead to entirely misleading results owing not only to changes in temperature and pressure, but also to the fact that the solution may be actively depositing scale minerals within the well. In addition, the

possible deposition of carbonate scale is dependent upon the carbon dioxide partial pressure in contact with the solution. The minerals that appear to pose the most serious problems in oilwell scaling are the sulfates of calcium and barium, and calcium carbonate. Calcium sulfate and calcium carbonate have solubility values that decrease with increasing temperature. The higher ambient temperature in the down-hole situation will therefore encourage the formation of scale deposits of these minerals. In the case of calcium sulfate the problem is complicated by the transition between the dihydrate, hemihydrate, and anhydrite phases. These calcium sulfate polymorphs may be stable or unstable under different conditions of temperature or of ionic strength. Barium sulfate presents a particularly serious problem; since it is very insoluble and cannot be dispersed once it has deposited as scale.

Numerous studies have been made of the spontaneous precipitation of sparingly soluble minerals from solutions containing concentrations of the crystal lattice ions considerably in excess of the solubility values. Attempts are usually made to use controlled methods of mixing the reagent solutions containing the lattice ions, but it is extremely difficult to obtain reproducible results from such experiments. There are probably no systems that are entirely free from foreign substances or dust particles that can readily act as sites for the formation of nuclei of the precipitating phase. The attainment of so-called "homogeneous" nucleation conditions is therefore very difficult even when extreme precautions are taken to exclude impurities and foreign particles from the solutions.<sup>1-3</sup> Experiments are frequently conducted to determine scaling thresholds in the laboratory by mixing solutions of salts containing the lattice ions and observing the appearance of the first precipitate. Such experiments are open to the same objections as those given above, however; moreover, they are frequently carried out in such a manner as to ignore important kinetic factors in the rate of precipitation. Thermodynamic interpretations of the results assume the attainment of equilibrium and involve the thermodynamic solubility products of the precipitating minerals. Often, the effects of ionic strength differences are entirely ignored and the thermodynamic solubility products are used indiscriminately without calculating the values of the activity coefficients under the conditions of

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the experiments.

The thermodynamic treatments outlined above assume that at all stages of the scaling processes the systems are effectively at equilibrium and are amenable to treatment with the experimentally measured solubility products. There are, however, important kinetic considerations that must be taken into account. Thus under certain conditions of ionic strength or of temperature the initially precipitating phase may be thermodynamically unstable and may transform to the stable phase during the course of the reaction. Moreover, the time scale in which such changes take place may be considerably longer than typical time intervals of interest under down-hole conditions. It is the prevention or control of scaling while the salt solutions are in contact with the well-drilling components that is of particular interest to the petroleum engineer. It will be evident from results presented in this paper that many of the commonly used scale inhibitors will prevent crystal growth or scale formation for only a rather specific time. At the end of this induction or delay period in the crystal growth reactions, the precipitation can take place at rates at least as high as those observed in the pure precipitating medium that contains none of the additive. This may be perfectly satisfactory in the field, provided that the induction period is longer than the time the salt solutions contact the oil-drilling equipment. All these factors militate against the accurate determination of threshold concentrations below which scaling will not occur under conditions in the field. The seriousness of the scaling problem depends not only upon the actual quantity of scale deposited, but also upon the crystal morphology of the precipitated phase. Some crystal shapes will pack together and form a serious scaling problem, whereas others can be readily swept away in the stream of salt solution contacting the surface. As we shall see, additives may have significant effects upon the morphology of the precipitating crystals. In addition, the possibility of epitaxial growth of one scaling phase upon another should not be overlooked.

As stated above, experiments concerned with scaling threshold and spontaneous precipitation are difficult to reproduce. A minute perturbation of any of the experimental conditions may have a dramatic effect upon the observed results. One of the main problems is that upon mixing two solutions, each of which contains one of the sparingly soluble salt lattice ions, both nucleation and growth occur simultaneously. It is difficult to determine whether all the crystal nucleation takes place initially before crystal growth, although this is frequently assumed in efforts to explain the experimental results in individual precipitating systems. It is likely that both the size and size distribution of the precipitating particles change continuously during the precipitation reaction, making it very difficult to analyze the experimental results.<sup>4,5</sup>

Provided that special precautions are taken to avoid local concentration effects and the presence

of foreign particles, it is possible to prepare stable solutions of most electrolytes of concentrations greater than that corresponding to the solubility value. The critical concentration, above which spontaneous precipitation takes place, is quite well defined and can often exceed the solubility value by a factor of 5 to 10. Practical methods of preparing such solutions include the careful mixing of reagent solutions containing the crystal lattice ions and the heating or cooling of saturated solutions of the salts. The resulting supersaturated solutions of the minerals of interest are stable for periods of days. The maximum solution supersaturation at 25°C and normal pressures which can be employed in seeded growth experiments are  $S = 1.0$  for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 2.0 for  $\text{CaCO}_3$  (calcite) and approximately 1.0 for  $\text{BaSO}_4$ . Here,  $S$  is defined as  $(m - m_o)/m_o$ , where  $m$  is the concentration of the salt and  $m_o$  is the solubility value. The stable supersaturated solutions are inoculated with well characterized seed crystals of the mineral under study. Then the rate of crystal growth is determined by following, as a function of time, the concentrations of lattice ions in the solution and the specific surface area of the growing crystals, and by microscopically examining the precipitates. Thus the rate of crystal growth can be studied without the added complications introduced by concomitant nucleation. Under some conditions, however, existing crystals may induce the formation of new crystals in a secondary nucleation process; this may constitute an important problem in the field.

In most of the crystal growth studies made in our laboratory, the seeded growth technique in stable supersaturated solutions has been adopted since, unlike spontaneous precipitation experiments, the results are perfectly reproducible. The effects of such factors as temperature and ionic strength, and the effectiveness of scale-inhibiting additives may therefore be studied quantitatively. Rates of crystal growth are determined by withdrawing solution aliquots from the crystallization cells and analyzing chemically, potentiometrically, conductometrically, spectrophotometrically, or by atomic adsorption spectrophotometry. In addition, the solid phases are examined both by optical and scanning electron microscopy, and surface areas are determined by the BET method. Typical plots of solution concentration against time are shown in Fig. 1 for the crystallization of calcium sulfate,<sup>6</sup> calcium carbonate,<sup>7</sup> and barium sulfate.<sup>8</sup> The addition of inoculating seed crystals at time zero induces crystal growth immediately, and this is characterized by a regular fall in solution concentration of lattice ions with time. Under certain conditions (Curve a) induction effects are observed and these will be discussed later.

#### CALCIUM CARBONATE

In the absence of induction effects, the rate of crystallization of a considerable number of sparingly

are stable concentrations solubility which qu well ility value methods of ful mixing tal lattice saturated rsaturated stable for supersatur- ch can be re  $S = 1.0$  lcite) and defined as ion of the The stable with well eral. under determined concentra- and the stals, and acipitates, be studied duced by onditions, formation a process; em the ade in our in stable ed since, nents, the effects of ength, and itives may Rates of ithdrawing cells and conducto- y atomic , the solid l scanning reas are l plots of shown in sulfate, 6 te. 8 The time zero d this is solution ne. Under ffects are er.

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soluble electrolytes of symmetrical charge type from supersaturated solutions has been found to follow equations of the type<sup>2,9-11</sup>

$$-\frac{dm}{dt} = k^+s(m - m_o)^2 \dots \dots \dots (1a)$$

$$-\frac{dT}{dt} = ks(T - T_o)^2 \dots \dots \dots (1b)$$

In these equations,  $m$  represents the concentration of free lattice ions in the supersaturated solution at time  $t$ , and  $T$  is the total metal concentration.  $m_o$  and  $T_o$  are the corresponding solubility values corrected to the ionic strength of the experiment,  $s$  is proportional to the number of growth sites present, and  $k^+$  and  $k$  are the corresponding rate constants. Fig. 1, Curve c, shows a typical growth curve for the crystallization from supersaturated solution on to calcite seed crystals. In the case of calcium carbonate, Eq. 1 may be written

$$-\frac{d[Ca^{2+}]}{dt} = ks(T_{Ca} - T_{Ca}^o)^2 \dots \dots \dots (2)$$

For the calculation of the concentrations of ions in the solutions, it is necessary to take into account each of the acid-base and ion-pairing equilibria.<sup>12</sup> The concentrations of all the ionic species in the supersaturated solutions can then be calculated from the experimental pH values using expressions for mass balance by successive approximations for the ionic strength,  $I$ .<sup>13</sup>  $T_{Ca}^o$  values are given by the sum of the concentrations of all the calcium-containing species at equilibrium. Throughout all our work discussed in this paper, activity

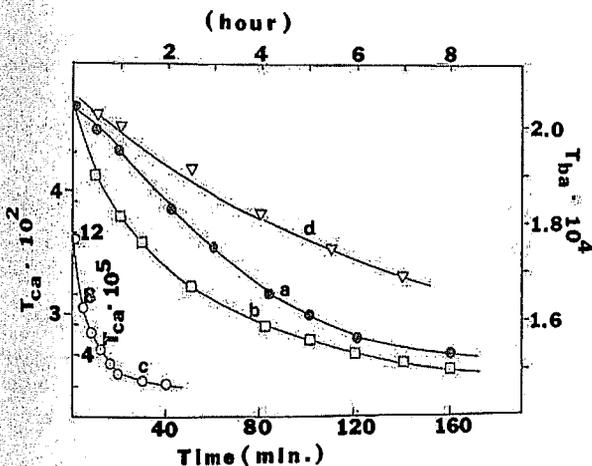


FIG. 1 — PLOTS OF METAL ION CONCENTRATION (CONC.) VS TIME AFTER THE ADDITION OF SEED CRYSTALS TO STABLE SUPERSATURATED SOLUTIONS AT 25°C. TOTAL CALCIUM ION CONC. (LEFT-HAND OUTER ORDINATE) VS TIME (LOWER ABSCISSA) FOR CALCIUM SULFATE GROWTH: CURVE a, ●, SEED CONC., 0.44 mg/ml; CURVE b, □, SEED CONC., 1.9 mg/ml. TOTAL CALCIUM ION CONC. (LEFT-HAND INNER ORDINATE) VS TIME (LOWER ABSCISSA) FOR CALCIUM CARBONATE GROWTH, CURVE c, ○, SEED CONC., 0.46 mg/ml. TOTAL BARIUM ION CONC. (RIGHT-HAND ORDINATE) VS TIME (UPPER ABSCISSA) FOR BARIUM SULFATE GROWTH, CURVE d, ∇, SEED CONC., 2 mg/ml.

coefficients,  $f_z$ , of  $z$ -valent ions have been calculated using the modification of the Debye-Hückel equation proposed by Davies<sup>14</sup>:

$$\log f_z = -Az^2 [I^{1/2}/(1 + I^{1/2}) - 0.3I]$$

Analysis of the calcite crystal growth data is facilitated by employing the integrated form of Eq. 2:

$$(T_{Ca} - T_{Ca}^o)^{-1} - (T_{Ca}^i - T_{Ca}^o)^{-1} = kst, \dots (3)$$

where  $T_{Ca}^i$  is the concentration of free calcium ions at zero time and  $T_{Ca}^o$  is the solubility value. The linear plot of  $(T_{Ca} - T_{Ca}^o)^{-1} - (T_{Ca}^i - T_{Ca}^o)^{-1}$  as a function of time shown in Fig. 2 confirms the applicability of Eq. 2 for the interpretation of the experimental results.

The observed second-order dependence of the rate of crystal growth upon the supersaturation (Eqs. 1 and 2) reflects the slow step or steps in the over-all crystal growth process in which hydrated lattice ions in the solution are transported to the crystal surface where they are dehydrated and incorporated into growing sites on the crystal surface. If the equilibrium at the crystal face is sufficiently rapid so as not to be involved in the rate-determining steps, the crystal growth would be controlled by the bulk diffusion of material up to the surface. In terms of a simple diffusion model, the rate of crystallization would then be expected to be proportional to the first power of the supersaturation or  $(T - T^o)$ . The observed second-order dependence points to a rate-limiting step involving a surface reaction at the crystal face. This may be adsorption,<sup>15</sup> surface diffusion,<sup>16</sup> or even dehydration of the lattice ions.<sup>17</sup> Further evidence for the proposed interfacial mechanism for calcite growth is provided

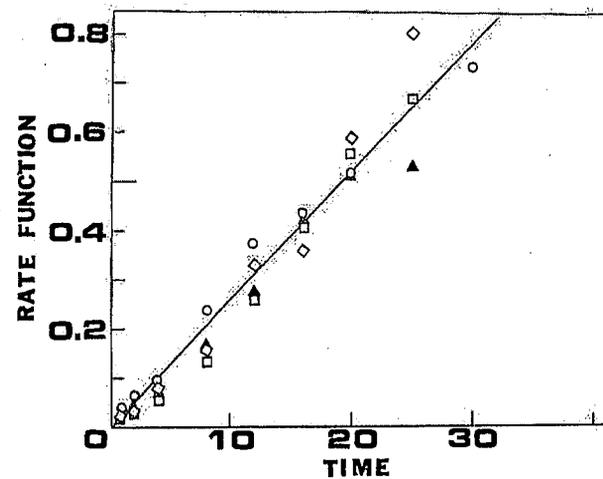


FIG. 2 — CALCIUM CARBONATE CRYSTAL GROWTH. PLOTS OF RATE FUNCTION,  $[(T_{Ca} - T_{Ca}^o)^{-1} - (T_{Ca}^i - T_{Ca}^o)^{-1}] \times 10^5$ , VS TIME (MIN.). EXPT. 32A, ▲; EXPT. 32B, ◇; EXPT. 34AII, ○. STIRRING RATE, 385 RPM; SEED CONC., 0.24 mg/ml; TEMP., 25°C; TOTAL CARBONATE CONC.,  $10^{-2}M$ ; TOTAL CALCIUM CONC.,  $10^{-4}M$ ; pH = 9.1.

by the observed insensitivity of the rate constant  $k$  to changes in the rate of stirring in the crystallization cell.<sup>7</sup>

A series of calcite crystal growth experiments was conducted at different temperatures between 10° and 40°C, and in each case, Eq. 2 satisfactorily fitted the experimental data. The activation energy for crystal growth calculated from the slope of the linear plot of  $\ln k$  against  $T^{-1}$  was 11.0 kcal mol<sup>-1</sup>. This value is considerably larger than the value to be expected for a diffusion-controlled reaction (~4.2 kcal mol<sup>-1</sup>), again pointing to the proposed interfacially controlled mechanism for calcium carbonate crystal growth. In actual scaling situations, the distinction between a liquid phase (bulk) diffusion control and a surface reaction control is an important one. For calcite, and indeed for all the important scale minerals discussed in this paper, the rate of crystallization is independent of the fluid dynamics of the system at least within the range of stirring rates (200 to 800 rpm) attainable in our crystallization experiments. It would therefore be expected that the rate of the scaling process would be very little affected by such factors as flow velocity of the loaded aqueous phases over the scaling surfaces.

#### BARIUM SULFATE

Barium sulfate scaling is frequently observed in oilfield operations where, owing to its exceptionally low solubility, it presents an acute problem. A number of studies have been concerned with nucleation and spontaneous growth, but the difficulty of obtaining reproducible results in such experiments has already been emphasized. Turnbull<sup>18</sup> examined the rate of precipitation of the salt by measuring the electrical conductivity. He concluded that all but a negligible number of nuclei were formed during the mixing process; the number of nuclei apparently depended upon the relative concentration of the precipitants, barium nitrate and potassium sulfate. Walton and Hlabse,<sup>19</sup> on the other hand, used a light-scattering technique to investigate the same precipitation and concluded that the number of nuclei was independent of the concentration of precipitants. On the basis of this finding, those authors suggested that nucleation was heterogeneous and took place on particles of impurities in the solution. Both interface control<sup>18</sup> and bulk liquid diffusion control<sup>20</sup> have been suggested for the subsequent growth process, and the confusion may be due to the difficulty in avoiding heterogeneous nucleation in experiments designed for purely homogeneous nucleation.

The conflicting results and theories for the precipitation of barium sulfate outlined above renders impossible the accurate prediction of barium sulfate precipitation in the field. As stated previously, the use of thermodynamic relationships in interpreting the results does not answer the important kinetic questions<sup>21</sup> as to how much time it will take to precipitate a given amount of barium sulfate and how and where the crystals will nucleate

and grow in a given system.

To avoid the complications introduced by possible heterogeneous nucleation, the kinetics of growth of well characterized seed crystals of barium sulfate from stable supersaturated solutions was studied in our laboratory some time ago.<sup>8</sup> Concentration changes were accurately monitored ( $\pm 0.01$  percent) by following the conductance of the solutions, and a typical growth curve is shown in Fig. 1 (Curve d) in the presence of a relatively high concentration of seed crystals (approximately 1 mg per milliliter of supersaturated solution), the rate of crystallization closely follows Eq. 1, indicating that the crystal growth process is once again controlled by a reaction at the crystal surface. This conclusion is supported by an observed growth rate that is insensitive to changes in the stirring rate of the conductance cell.<sup>8</sup>

In supersaturated solutions containing nonequivalent concentrations of lattice ions, Eq. 4 satisfactorily represents the experimental data.<sup>8</sup>

$$\frac{-dN}{dt} = k's'N^2 \quad (4)$$

In this equation,  $N$  is the number of moles l<sup>-1</sup> of salt to be deposited before equilibrium is reached, and  $k'$  and  $s'$  are corresponding rate-constant and growth-site terms, respectively, analogous to those in Eq. 1.

Under conditions in which the supersaturation is raised or the amount of seeding crystals is reduced, the barium sulfate rate curve (Fig. 1, Curve d) is characterized by an initial growth surge for up to 30 percent of the reaction, after which the rate conforms to the regular quadratic kinetic equation, Eq. 1. It appears that secondary nucleation takes place during this growth surge,<sup>8</sup> and scanning electron microscopic studies are presently under way to examine this phenomenon in more detail.<sup>22</sup> The results of the barium sulfate seeded growth studies show that, as with calcium carbonate, the rate of crystal growth does not depend upon the fluid dynamics of the precipitation system. This is of great importance in trying to understand barium sulfate scaling in the field. There is still a dearth of information concerning the effects of brine concentrations upon the rate of crystal growth<sup>21</sup> of barium sulfate. Studies are presently under way in our laboratory to determine the influence of ionic strength and of the commonly applied scale inhibitors upon the rate of crystallization.<sup>22</sup>

#### CALCIUM SULFATE

Calcium sulfate scaling causes severe problems under down-hole conditions in many oil fields.<sup>23</sup> Not only does a rise in temperature promote scaling through a decreasing solubility, but phase equilibria must also be taken into account. A number of studies of the seeded crystal growth of calcium sulfate dihydrate have been made in our laboratory and typical growth curves representing the change in calcium concentration in the supersaturated

solution with time are shown in Fig. 1 (Curves a and b).<sup>6</sup> It can be seen in Fig. 3 that in the absence of induction effects (Curve b), the rate of crystal growth closely follows Eq. 1. As in the crystal growth of calcium carbonate and barium sulfate, this evidence, together with the demonstrated absence of stirring effects,<sup>6</sup> points to a crystal growth process that is dependent upon a reaction or reactions taking place at the crystal surface. It is very interesting to note that for calcium sulfate dihydrate, unlike for the other two systems, the mass of mineral deposited during experiments such as those illustrated in Fig. 1, is as much as two or three times the weight of seed crystals added initially. This is reflected in a considerable increase in surface area of the crystallites. The kinetic equation, Eq. 1, however, satisfactorily describes the growth data (Fig. 3) without having to take into account this increase in surface area. In Eq. 1,  $s$  represents the number of growth sites added as seed crystals, and in experiments employing different amounts of seeding crystals, the rate constant is directly proportional to the quantity of crystals added initially.<sup>6</sup> These results are consistent with the idea that no new growth sites are formed during crystallization. Such would be the case if growth were confined to the screw dislocations present on the seed crystals.

When the amount of seed crystal is reduced (Fig. 1, Curve a) or the supersaturation is increased, crystal growth of calcium sulfate is preceded by an induction period. Microscopic studies of the growing crystals clearly indicate<sup>6</sup> that the appearance of the induction period is accompanied by secondary nucleation. Unlike the regularly growing crystals in the experiment represented by Fig. 1, Curve b, the crystals corresponding to Curve a show considerable surface roughening characteristic of surface nucleation. The existence of secondary nucleation has been recognized for

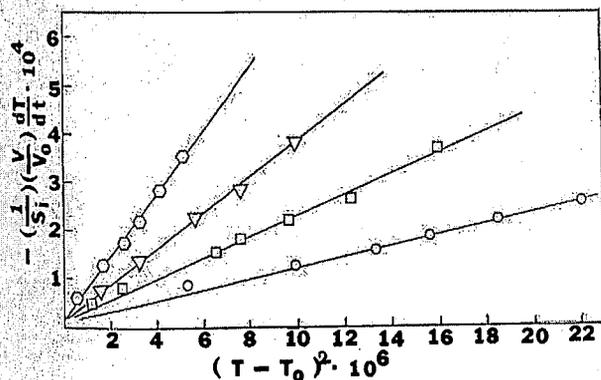


FIG. 3 — CALCIUM SULFATE DIHYDRATE CRYSTAL GROWTH. PLOTS OF  $-(1/S_i)(V/V_0)(dV/dt) \times 10^4$  VS  $(T-T_0)^2 \times 10^6$ , WHERE  $S_i$  IS THE INITIAL SEED CRYSTAL CONC.,  $V_0$  THE INITIAL VOLUME OF SOLUTION, AND  $V$  THE VOLUME OF SOLUTION OF TIME  $t$ . EXPT. G37,  $\circ$ , TEMP., 100°C; INITIAL SEED CONC., 0.17 mg/ml; EXPT. G43,  $\nabla$ , TEMP., 90°C; INITIAL SEED CONC., 0.28 mg/ml; EXPT. G62,  $\square$ , TEMP., 80°C; INITIAL SEED CONC., 0.29 mg/ml; EXPT. G64,  $\circ$ , TEMP., 70°C; INITIAL SEED CONC., 0.32 mg/ml.

some time by those interested in industrial crystallization, but it is only relatively recently that it has been invoked in kinetic studies of crystal growth.<sup>24</sup> Under conditions in which the rate of growth is rapid, the seed crystals may grow as a polycrystalline mass that breaks up to provide additional crystals for growth. Alternatively, the secondary nucleation may be due to collision breeding in which large numbers of seed crystals may be formed when the seed particles collide with each other or slide over the surfaces of the crystallization cell.

The growth of calcium sulfate phases at elevated temperatures is of considerable importance to the petroleum engineer. In our laboratory we have developed an autoclave for the study of crystal growth and dissolution at temperatures at and above 100°C.<sup>25</sup> Using this apparatus, it is possible to make the same carefully controlled seeded crystal growth experiments as at room temperatures, and both solution and solid phases can be sampled and analyzed without subjecting them to decreased ambient temperatures during the sampling procedure. It can be seen in Fig. 3, that Eq. 1 satisfactorily represents the growth results for the dihydrate salt over a wide range of temperature up to 100°C. The value of the activation energy 15.0 kcal mol<sup>-1</sup>, for crystal growth calculated from the temperature dependence of the slopes of the lines, supports the proposed surface-controlled mechanism.

At temperatures near 100°C, a calcium sulfate phase transition involving the dihydrate and hemihydrate takes place (see Fig. 4). In Fig. 5 is shown a typical crystal growth experiment at 105°C in which calcium sulfate dihydrate seed crystals were used. It can be seen that the solution concentration approaches the hemihydrate solubility value (Curve a) rather than that of the dihydrate after about 50 minutes. Photomicrographs of the crystal during the experiment clearly show that during the reaction, in addition to an increase in size of the added dihydrate seed crystals, small crystallites of the hemihydrate are formed. The presence of both phases is confirmed by X-ray powder diffraction. At the completion of the experiment at 105°C the crystalline phase in the autoclave consisted entirely of the hemihydrate. It is clear that the phase transformation does not take place in the solid phase, but the nucleation of the hemihydrate occurs through a secondary nucleation mechanism probably involving collision breeding of the nuclei. This is followed by a dihydrate dissolution-hemihydrate growth process (Fig. 4). It is important to note that in the dihydrate-hemihydrate transformation, the rate of formation of the more stable phase in these seeded growth experiments markedly increases with solution supersaturation. In none of the experiments at elevated temperatures was the anhydrite phase observed, despite the fact that thermodynamically the anhydrite was the stable phase. The mechanism of crystal growth of the anhydrite and the effect of various brine concentrations upon both the growth process and the phase

transformations are presently being investigated in our laboratory.

### SCALE INHIBITION

One method of solving scaling problems is to remove the scale-forming ions from the aqueous systems. However, the cost of chemical treatment of the large volumes of water involved is almost prohibitive. Moreover, this method cannot be used to solve scaling problems in inaccessible down-hole situations. Several years ago in a seeded growth study of the crystallization of the sparingly soluble salt strontium sulfate, it was observed that when the solutions were prepared with deionized water, the rate of growth of seed crystals was very slow, and the crystallization reaction ceased completely at less than 25 percent completion! These effects were removed by the use of double-distilled water and it became clear that the ion-exchange resins used for the preparation of the deionized water were the source of the minute traces of impurity in the water. Thus extremely low concentrations of impurity were effective in almost completely inhibiting the crystal growth reaction. The use of such inhibitors provides a very attractive method for the control of scaling, and a substantial number of potential additives have been investigated.<sup>26-29</sup>

The seeded growth technique enables reproducible crystallization rate experiments to be carried out in the presence of additives. The additives are added to the stable supersaturated solutions before the inoculation with seed crystals, and the subsequent crystal growth reaction is monitored in the usual manner. The following factors must be taken into account in analyzing the results of such experiments.

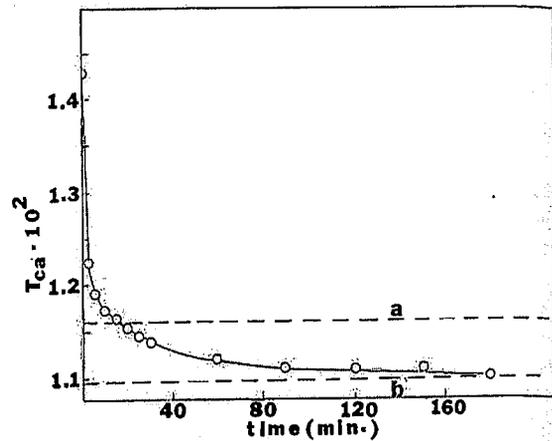


FIG. 5 — CALCIUM SULFATE DIHYDRATE CRYSTAL GROWTH AND PHASE TRANSFORMATION. PLOT OF TOTAL CALCIUM ION CONCENTRATION AS A FUNCTION OF TIME AFTER THE ADDITION OF 104 mg OF CALCIUM SULFATE DIHYDRATE SEED CRYSTALS TO A SUPERSATURATED SOLUTION (TOTAL VOLUME 850 ml) AT 4 ATM AND 105°C. THE SOLUBILITY OF CALCIUM SULFATE DIHYDRATE AT 105°C IS  $1.16 \times 10^{-2}$  (LINE a), AND THAT FOR CALCIUM SULFATE HEMIHYDRATE IS  $1.095 \times 10^{-2}$  M (LINE b).

1. The additive may form stable complexes with one of the crystal lattice ions of the precipitating phase. The effective concentration of the free ions would therefore be reduced and the solubility increased.

2. The additive may be adsorbed at the growth sites and thus prevent further precipitation. If the adsorption takes place only at certain sites, the morphology of the growing crystals may be grossly changed.

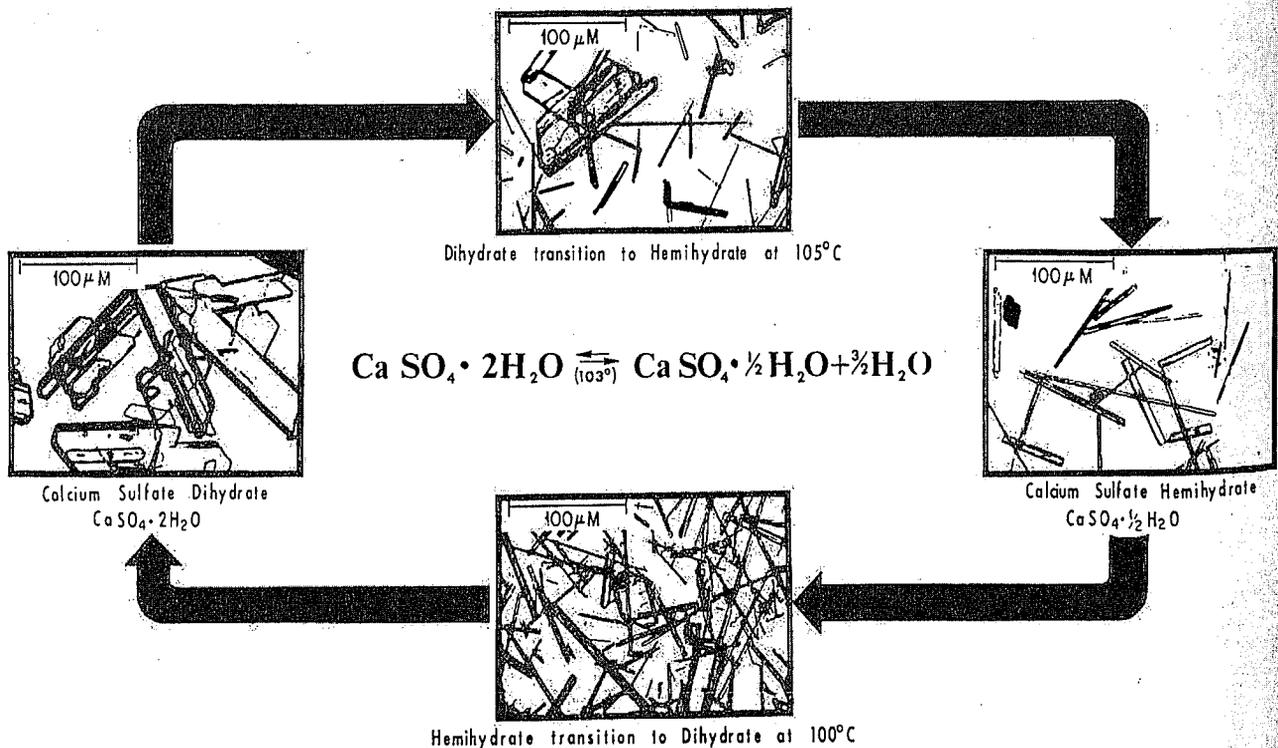


FIG. 4 — CALCIUM SULFATE PHASE TRANSITION NEAR 100°C.

3. The additive, if ionic, will influence the ionic strength of the solution and hence the effective solubility of the precipitating phase. In the examples to be discussed in this paper, the concentration of additives is so low that this effect is negligible.

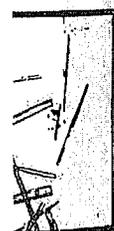
The organic phosphonates have been found to be particularly effective in inhibiting scale formation,<sup>28,29</sup> and a number of studies have been made of their influence on the rate of crystal growth of calcite.<sup>30</sup> The additives studied, kindly made available by T. M. King, Monsanto Co., included *N, N, N', N'* ethylenediaminetetra-(methylenephosphonic) acid (ENTMP, Dequest-2041®), *N, N, N', N'* triethylenediaminetetra(methylenephosphonic) acid (TENTMP, Dequest-2051®), nitrilotri(methylenephosphonic) acid (NTMP, Dequest-2001®) and 1-hydroxyethylidene 1, 1-diphosphonic acid (HEDP, Dequest-2011®). Typical growth curves of calcite seed crystals with and without ENTMP are shown in Fig. 6. These curves clearly demonstrate the marked growth inhibition in the presence of the phosphonate; at a concentration of only 0.5 ppm or  $\sim 1 \times 10^{-6}$  mol l<sup>-1</sup> the reaction is almost completely stopped. In a comparative study, the effectiveness of the phosphonate inhibitors at a concentration level of 0.5 ppm was found to be HEDP > TENTMP > ENTMP > NTMP. In Fig. 6, growth curves are presented over a wide range of ENTMP concentrations. It can be seen in Fig. 7 that the rate law represented by Eq. 2 in pure supersaturated solutions is also applicable to calcite crystal growth in solutions containing a range of phosphonate concentrations. The marked inhibiting effect is also illustrated in Fig. 8, where the rate constants obtained from the slopes of the plots in Fig. 7 are plotted as a function of ENTMP concentration. At additive concentration levels of 10<sup>-6</sup>M, considerably less than 1 percent of the effective crystal seed

surface will be covered by the added phosphonate despite almost complete inhibition of the growth reaction. This indicates that a relatively small number of growth sites are active in the crystallization process, which is consistent with a screw dislocation mechanism. If it is assumed that the additive molecules are adsorbed on growth sites on the surface of the crystals, their presence will prevent deposition of material near those growth sites. The relative decrease in the rate constant may therefore be interpreted in terms of a decrease in effective crystal surface area, and it is found that the experimental data are consistent with a

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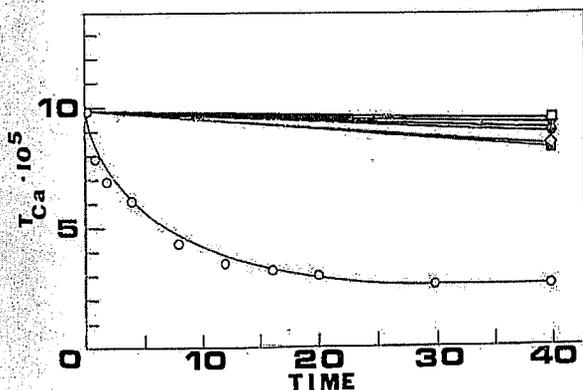


FIG. 6 — GROWTH OF CALCITE SEED CRYSTALS IN THE PRESENCE AND ABSENCE OF ENTMP. PLOTS OF TOTAL CALCIUM ION CONCENTRATION AS A FUNCTION OF TIME (MIN) ○, EXPT. 34AII; ◇, EXPT. 34C, 2.5 PPM ENTMP; □, EXPT. 34E, 2.5 PPM TENTMP; ◆, EXPT. 34AA, 0.5 PPM ENTMP; ●, EXPT. 34BB, 0.5 PPM TENTMP; △, EXPT. 34CC, 0.5 PPM HEDP; ■, EXPT. 34DD, 0.5 PPM NTMP. STIRRING RATE, 385 RPM; SEED CONC., 0.46 mg/ml; TEMP., 25°C; TOTAL CARBONATE CONC., 10<sup>-2</sup>M; TOTAL INITIAL CALCIUM CONC., 10<sup>-4</sup>M; pH = 9.1.

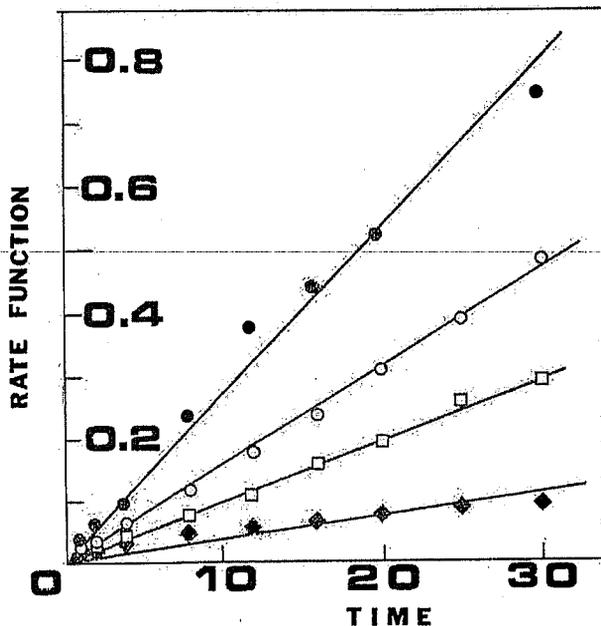


FIG. 7 — CALCITE CRYSTAL GROWTH IN THE PRESENCE OF ENTMP. PLOTS OF THE RATE FUNCTION,  $[(T_{Ca} - T_{Ca}^0)^{-1} - (T_{Ca}^i - T_{Ca}^0)^{-1}] \times 10^5$  VS TIME (MIN) ●, EXPT. 43AII, 0 PPM ENTMP; ○, EXPT. 34AAA, 0.5 PPM ENTMP; □, EXPT. 34AAC, 0.08 PPM ENTMP; ◆, EXPT. 34AAB, 0.12 PPM ENTMP. STIRRING RATE, 385 RPM; SEED CONC., 0.46 mg/ml; TEMP., 25°C; TOTAL CARBONATE CONC., 10<sup>-2</sup>M; TOTAL INITIAL CALCIUM CONC., 10<sup>-4</sup>M; pH = 9.1.

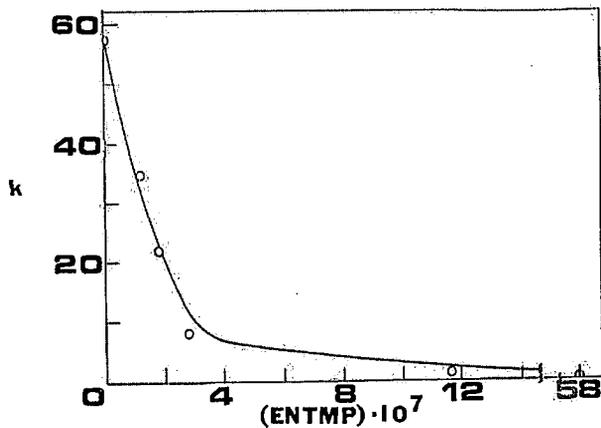


FIG. 8 — CALCITE CRYSTAL GROWTH IN THE PRESENCE OF ENTMP. RATE CONSTANTS OBTAINED FROM DATA IN FIG. 7 PLOTTED AGAINST ADDITIVE CONCENTRATION (ENTMP).

simple Langmuir-type adsorption isotherm.<sup>30</sup>

Concentration levels of ENTMP that inhibit calcium carbonate seeded crystal growth also induce a modification in calcium carbonate crystal habits. Habit modification was studied by a spontaneous precipitation procedure. Induction periods ( $t_i$ ) for spontaneous precipitation were taken as the time between solution mixing and the onset of turbidity. Crystal habit was observed using a Unitron Series N microscope with a Mirex camera. Calcite precipitated from pure supersaturated solutions exhibited a uniform rhombohedral morphology to a calcium carbonate concentration of at least  $5 \times 10^{-3}M$  (see Fig. 9a). Results of spontaneous precipitation experiments are summarized in Table 1, and photomicrographs of spontaneously precipitated calcium carbonate prepared in the presence and absence of ENTMP are shown in Fig. 9.

Increases in observed induction times for spontaneous precipitation in the presence of 1.0 ppm ENTMP compared with those in its absence suggest that ENTMP inhibits both nucleation and crystal growth of calcium carbonate. At the lowest

TABLE 1 — INDUCTION PERIODS AND MORPHOLOGIES FOR CALCIUM CARBONATE SPONTANEOUSLY PRECIPITATED IN THE PRESENCE AND ABSENCE OF ENTMP\*

Experiment Number	ENTMP (ppm)	$t_i$	Morphology
A1	0	< 5 seconds	uniform rhombohedral
A2	0.1	< 5 seconds	distorted rhombohedral
A3	1.0	~ 30 seconds	
A4	10.0	~ 2 minutes	irregular

\*Initial total calcium ion and total carbonate molarities were  $5 \times 10^{-3}$ .

ENTMP concentration (0.1 ppm) there was little significant difference between the induction time and the crystal morphology for the solutions with and without ENTMP (Table 1 and Figs. 9a and 9b). At higher concentrations, pronounced induction periods were accompanied by marked changes in precipitate morphology (Figs. 9c and 9d). The precipitate formed in this experiment was examined from time to time using X-ray powder diffraction techniques, and it was found that the precipitate

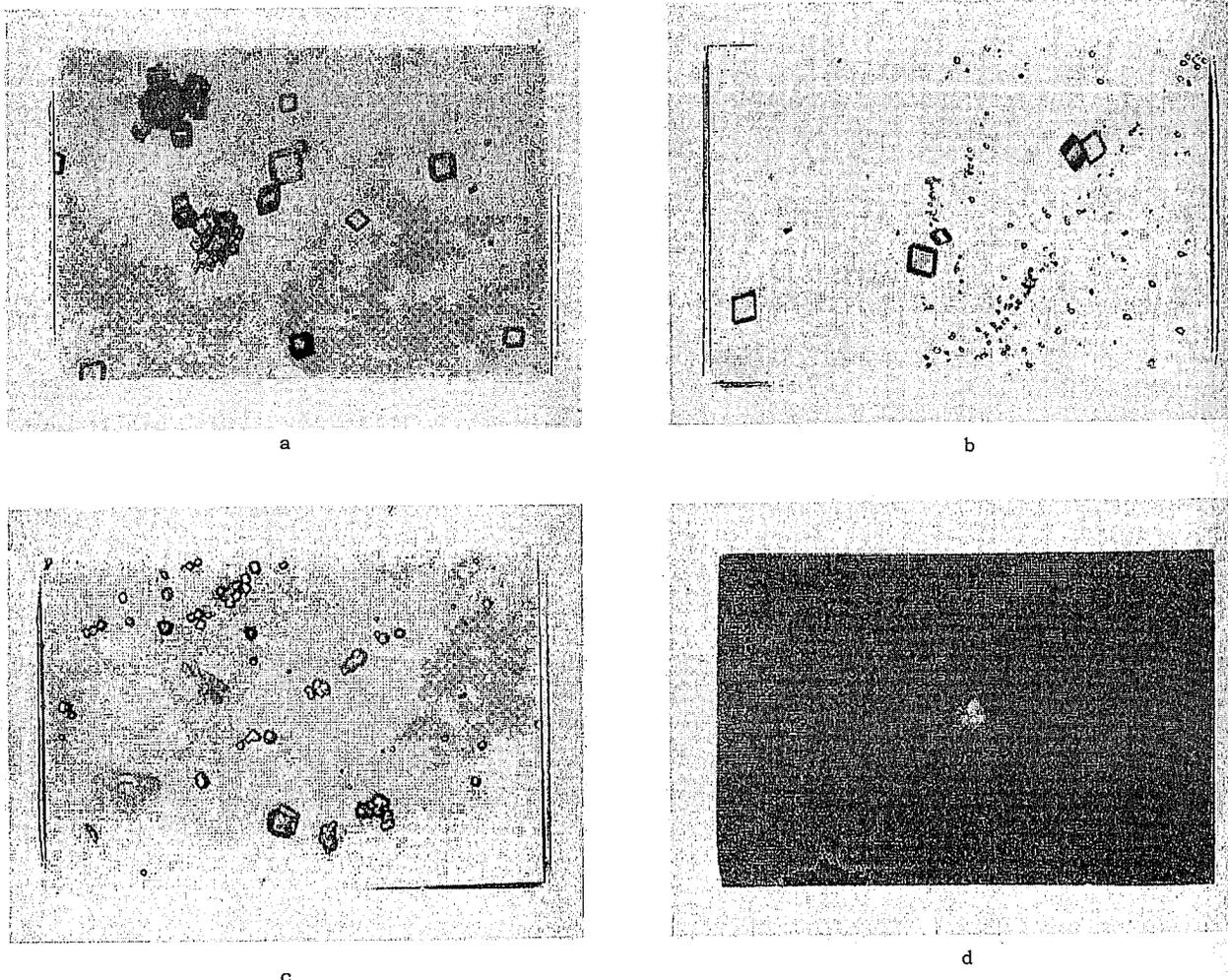


FIG. 9 — PHOTOMICROGRAPHS ( $\times 400$ ) OF CALCIUM CARBONATE CRYSTALS OBTAINED BY SPONTANEOUS PRECIPITATION AT  $25^{\circ}C$  FROM SOLUTIONS CONTAINING  $5 \times 10^{-3}M$  CALCIUM CARBONATE AND  $1 \times 10^{-2}M$  SODIUM CHLORIDE: a, 0.0 PPM ENTMP, 40 MINUTES AFTER MIXING SOLUTIONS; b, 0.1 PPM ENTMP, 40 MINUTES AFTER MIXING SOLUTIONS; c, 1.0 PPM ENTMP, 40 MINUTES AFTER MIXING SOLUTIONS; d, 10.0 PPM ENTMP, 18 HOURS AFTER MIXING.

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consisted of a mixture of calcium carbonate polymorphs, predominantly calcite with some vaterite and aragonite. At the highest ENTMP concentration there was no evidence of the rhombohedral calcite morphology characteristic of spontaneous precipitation in solutions without ENTMP (compare Figs. 9a and 9b). In these experiments, crystallization and recrystallization processes caused continuous changes in the precipitate morphology up to 3 weeks after the initial precipitate had formed. X-ray powder diffraction analysis of this precipitate showed that it consisted mainly of calcite with traces of vaterite.

A quantitative analysis of data presented in Table 1 is inappropriate because of the difficulty of distinguishing heterogeneous and homogeneous nucleation and of distinguishing nucleation from crystal growth in these experiments. In addition, during the spontaneous precipitation experiment changes may occur in both the surface area and the polymorphic composition of the solid formed. These difficulties are eliminated with a seeded growth technique. The results of the spontaneous precipitation studies of calcium carbonate in solutions containing ENTMP clearly indicate that ENTMP concentrations of about 1 ppm or greater in solution induce marked morphological and polymorphological changes in calcium carbonate nucleation and crystal growth. These effects are consistent with the adsorption mechanism proposed for the interpretation of ENTMP inhibition of calcite crystal growth.

In the case of calcium sulfate crystal growth, additives such as gelatin have much the same inhibiting effect as has ENTMP with calcium carbonate.<sup>31</sup> Eq. 1 satisfactorily interprets the rate data at concentrations of gelatin ranging from 1 to 100 ppm, and the decrease in rate constant can again be interpreted in terms of adsorption of additive at the growing crystal surface. However, the influence of the organic phosphonates upon calcium sulfate crystal growth appears to be strikingly different from that observed in the case of calcium carbonate. ENTMP and TENTMP at concentrations in the region of  $1 \times 10^{-6}$  mol l<sup>-1</sup> can effectively block all the active growth sites and hence bring the reaction to a complete stop. However, after a rather well defined induction period at 25°C and ranging from 0.5 to 7.5 hours for [TENTMP] from  $6 \times 10^{-7}$  to  $1.9 \times 10^{-6}$  mol l<sup>-1</sup>, respectively, growth of calcium sulfate takes place at rates comparable with those observed in the absence of additives.<sup>22</sup> Moreover, the duration of the induction period increases with increasing additive concentrations and shows a marked decrease as the temperature of the crystallizing system is raised.

This marked difference in the effect of phosphonates upon the crystal growth of calcium carbonate and calcium sulfate is of considerable importance in predicting scaling patterns in the field. In the case of calcium sulfate, it is essential

to ensure that appropriate additive concentrations are used so that the induction period in the precipitation reaction is sufficient to prevent scaling. It appears that at the end of the period completely uninhibited crystal growth can take place. Another important factor to consider is the relative effects of the scale inhibitors upon the nucleation and the growth reactions. There is evidence that the additive adsorption may reduce the critical free energy for two-dimensional nucleation, causing an increase in surface nucleation.<sup>11,32</sup>

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