Polymorphism of $CaCO_3$ Precipitated in a Constant-Composition Environment

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Polymorphism of calcium carbonate was investigated using a constant-composition method, and three polymorphs—calcite, aragonite, and vaterite—are produced. Factors that affect the formation of polymorphs are studied over a wide range, including solution pH, temperature, concentration ratio of components, supersaturation, ionic strength, and type and concentration of additives. At room temperature, solution pH is the most significant factor, and high yield polymorphs are present at different pH values. At a high temperature, aragonite becomes the major product at a pH below 12. The effects of the additive are complicated, depending on its type and concentration as well as the operating conditions. The influence of concentration ratio and supersaturation on the formation of polymorphs is less significant. Besides, various particle morphologies of $CaCO_3$ polymorphs are observed, depending on the operating conditions.

Introduction

To prepare functional particulate materials in the precipitation processes, the control of operating variables is crucial for tailoring the crystal form (polymorphism) and shape (morphology), which are important to the properties and performance of the products if further processing is to be done. When the precipitation results from the rapid crystallization of a barely soluble substance, with the supersaturation generated by chemical reaction, the operating variables, such as solution pH, temperature, solution composition, and type and concentration of additives, need to be considered. Among the barely soluble substances, calcium carbonate is the most studied system because the precipitation of calcium carbonate is a widely occurring process in nature as well as an important operation in industry. It is estimated that 7% of the earth's crust, as marble or limestone, is made of calcium carbonate. In the chemical industry, a large quantity of calcium carbonate is used as inorganic fillers for paper, plastics, rubber, and other materials, but different uses demand different physical and chemical properties. Calcium carbonate nucleates in three crystalline forms—calcite, aragonite, and vaterite—and in different particle morphologies or shapes for the polymorphs. Although calcite is more stable than other polymorphs at ambient temperature and atmospheric pressure, precipitates may be found as a mixture of polymorphs or with one of the forms predominating. Several experimental techniques have been employed in studying the crystal polymorphism and morphology, such as the free-drift method, pH-stat method, MSMPR crystallizer, and constant-composition method. Among them the constant-composition method is more advantageous as far as the control of operating variables is concerned.

The effects of operating variables on the polymorphs of calcium carbonate have been studied by a number of authors. Using the free-drift method, that is, by mixing calcium nitrate and sodium carbonate solutions without controlling the solution pH and composition during the course of precipitation, Wray and Daniels (1957) studied the effects of temperature, initial concentration of solutions, and aging time on the formation of polymorphs. A general trend was found for the effect of temperature and aging, respectively; higher temperature favors the formation of aragonite, and aging promotes the formation of calcite. In the study of precipitation caused by the contact of carbon dioxide with a solution containing calcium ion, Yagi et al. (1984) found that vaterite formed at low Ca^{2+} concentration. The result contradicted that reported by Roques and Girou (1974), who found that vaterite was produced at low temperature and high Ca^{2+} concentration. Kralj et al. (1990) produced nearly pure vaterite in the pH range from 8.5 to 10.0, using the free-drift method, with the initial relative supersaturation between 6.5 and 8.5. Hostomsky and Jones (1991) conducted experiments to study the precipitation of calcium carbonate in a continuous-flow crystallizer wherein they mixed aqueous solutions of calcium nitrate and sodium carbonate at 25°C. The crystal form of the precipitates depends on the concentration of reagents, the solution pH, and the residence time. Agglomerates of spherical vaterite particles were observed at pH ≥ 9.5. At a residence time of 20 min and a pH of 10.5, the agglomerates were made up of thin hexagonal vaterite platelets. Agglomerates of calcite rhombs appeared at a pH of 8.5. Xyla et al. (1991) used a plethostatic experimental approach to study the precipitation of calcium carbonate under the operating conditions of pH between 8.0 and 9.0 and the temperature between 25 and 80°C. They were able to identify vaterite as the crystalline phase formed initially at high supersaturation and then converted into the thermodynamically stable calcite. Vaterite formation could be identified only at conditions of sustained supersaturation. Recently, Tai and Chen (1995) tried to find the formation regions of the polymorphs on a supersaturation-pH diagram, which is not complete as far as the operating variables are concerned. Besides the influence of solution properties, the formation of $CaCO_3$ polymorphs depends largely upon the presence of impurities. For example, Mg^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+} favor the formation of aragonite (Koutsoukos, 1993; Söhnel and Mullin, 1982), whereas Mn^{2+}, Ca^{2+}, and Pb^{2+} favor calcite (Roques and Girou, 1974).

Although numerous studies of the polymorphism of calcium carbonate have been reported, the favorable conditions for each polymorph are generally unknown. This is because the operating variables were not controlled and changed during an experimental run in most of the studies. Besides, factors that influence the crystal forms interact; for example, a decrease in solution pH would cause a decrease in supersaturation. As a result, the precipitates contain a mixture of polymorphs, which means that the favorable conditions for the formation of each polymorph cannot be identified. In this study a constant-composition method is used to demonstrate the possibility of showing the effect of an isolated factor while keeping the other operating variables constant. A $CaCl_2/Na_2CO_3$ reacting system was performed without seeding in a semibatch crystallizer to search for the operating conditions, including solution pH, initial solution composition, temperature, and type and concentration of additive, that would favor the three polymorphs of calcium carbonate in aqueous solution.

Experimental Studies

Constant-composition technique

In this study the constant-composition method used to investigate the crystal morphology is essentially the same as that developed by Kazmierczak et al. (1982) for crystal growth. In an experimental run, the pH and composition are maintained constant by adding the titrant solutions of calcium chloride and sodium carbonate into the crystallizer simultaneously. Sodium chloride or potassium chloride is used to adjust the ionic strength of the solution. During the operation, the potential difference between the ion selective electrode (or glass electrode for measuring pH) and the reference electrode is measured and is maintained at a preset value. The measured voltage can be expressed by the Nernst equation as follows:

$$E = E' - 2.303(RT/z_iF)\log a_i, \tag{1}$$

where E' is a temperature-dependent constant; R is the gas constant; T is the absolute temperature; z_i the valence of species i; F the Faraday constant; and a_i the ionic activity.

At 25°C, Eq. 1 can be rewritten as

$$E = E' - 59.0\text{pH} \tag{2}$$

for a pH electrode and

$$E = E' - 29.6\text{pCa} \tag{3}$$

for a calcium ion selective electrode.

The detectable potential difference of the ion/pH meter is 0.1 mV, which corresponds to a change in pH of 0.0017 or a change in pCa of 0.0038. In this study, a change in pH of 0.01 has no effect on the polymorphism and morphology of calcium carbonate. Therefore, the constant-composition technique is suitable for the calcium carbonate system.

When the pH value is higher than 12.5, the major carbon species in the solution is CO_3^{2-} and the amount of CO_2 absorbed from air is not negligible. This messes up the control of constant composition. On the other hand, pH values below 8 give a low nucleation rate of calcium carbonate because only a trace amount of carbonate is present at low pH values. Therefore, the constant-composition experiments of calcium carbonate were operated in a pH range between 8 and 12.5 in this study.

Crystallization system

A crystallization system of the constant-composition technique for producing the $CaCO_3$ polymorphs is shown in Figure 1. The apparatus consists of a pH/ion meter (Metrohm 692), an impulsomat (Metrohm 614), a dosimat (Metrohm 665), an acrylic crystallizer, and a constant-temperature water bath. The geometry and size of the crystallizer and agitator are referred to a previous study (Tai and Chen, 1995). Since the solution pH, temperature (t), supersaturation (σ), and concentration ratio of T_{CA}/T_{CO_3} (r) are the operating variables chosen in this study, the desired initial concentration of $CaCl_2$ and Na_2CO_3 was estimated by successive approximation of the ionic strength, using a computer program that contains mass-action equations, mass-balance equations, charge-balance equations and the modified Debye–Hückle equation (Nancollas, 1966; Tai et al., 1993). Before an experimental run, the electrodes were standardized with buffers of pH 7.0, 9.0, and 13.0. In the calculation of σ, the solubility of calcite was used although the polymorphs of calcium carbonate have different solubility (Plummer and Busenberg, 1982). The supersaturation σ proposed by Nielsen and Toft (1984) is given by

$$\sigma = (IP/K_{sp})^{1/2} - 1, \tag{4}$$

where IP is the ionic product, defined as $IP = a_{Ca^{2+}} a_{CO_3^{2-}}$ for this system, and K_{sp} is the solubility product of $CaCO_3$. The activity of a species is the product of activity coefficient and concentration. Then the activity coefficient of z_i–valence species, y_{z_i}, is calculated by the modified Debye–Hückle equation:

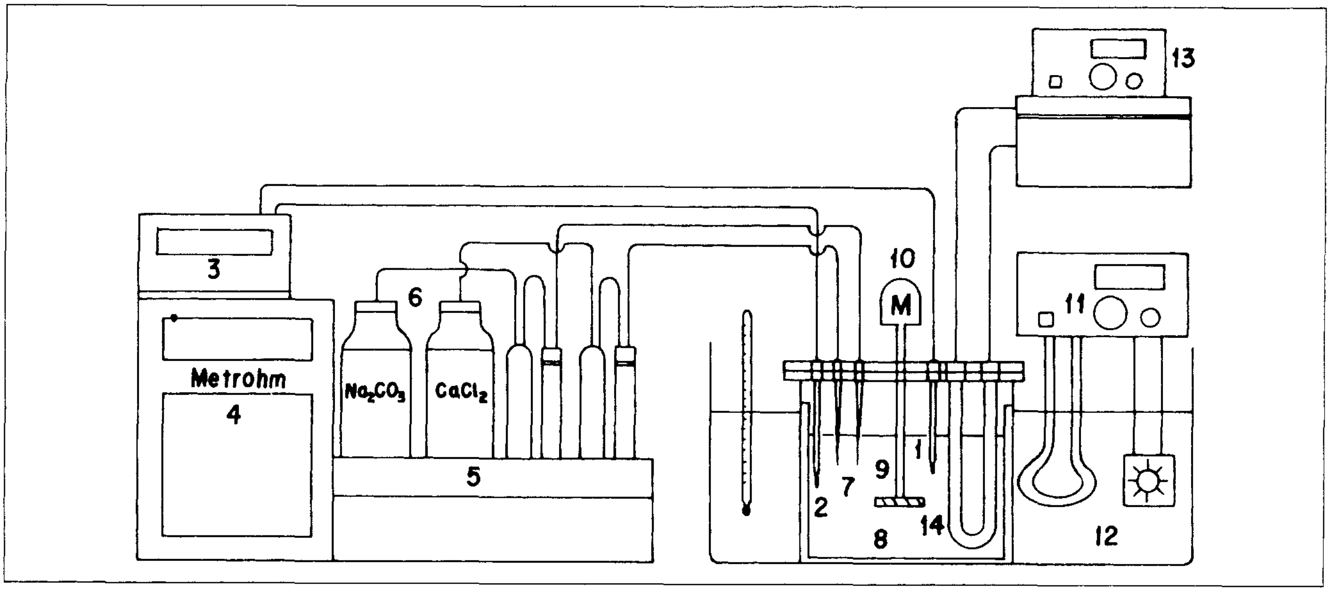

Figure 1. Crystallization system of the constant-composition experiment.

1. Combined pH glass electrodes; 2. calcium ion—selective and reference electrodes; 3. pH/ion meter; 4. impulsomat; 5. dosimat; 6. reagent bottle and delivery line; 7. burette; 8. crystallizer; 9. axial-flow impeller; 10. motor; 11. temperature controller; 12. water bath; 13. constant-temperature water bath; 14. U-tube.

$$\log y_{z_i} = -0.509 z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right), \tag{5}$$

where I is the ionic strength, $I = 1/2 \sum_{i=1}^{n} z_i^2 C_i$.

The crystallizer was placed in a thermostatic water-bath. One liter of supersaturated solution was prepared by mixing the calcium chloride and sodium carbonate solutions of known concentration in the crystallizer. The stirring rate was set at 800 rpm and the solution pH was adjusted to the desired value by adding a solution of 0.1 M NaOH or 0.1 M HCl. The induction periods appeared in most experimental runs with low production rates and were recorded. Once the calcium carbonate started to precipitate, the solution pH and concentration were maintained constant by adding the required amount of calcium chloride and sodium carbonate solutions simultaneously into the crystallizer. In some experimental runs of high supersaturation, the precipitation took place immediately after the solutions were mixed. In this case, the composition and pH were difficult to maintain constant, and the operation became the free-drift mode. The operating time varied from 5 min to 4 h, depending on the production rate of the precipitates. At the end of an experiment, the resultant slurry was filtered and the solids were dried at 70°C for 12 h. The dried products were then examined by a scanning electronic microscope (Hitachi S-2400) and X-ray powder diffractometer (MAC Science MXP-3 TXJ-7266) for crystal morphology and composition, respectively. The percentage of polymorphs in a product mixture was determined by direct linear analysis, as suggested by Klug and Alexander (1974). The X-ray powder diffraction patterns of $CaCO_3$ polymorphs produced in this experiment are shown in Figure 2.

Results and Discussion

Titration curves and solution composition

Using a pH-electrode as sensor, the titration curves obtained in the constant-composition operation, for example, are shown in Figure 3. In the figure, the point where the slope of the titration curve changes sharply is the induction period; for example, the induction period of run m-3 is about 2,000 s. Thus, the induction period for the solution of a higher pH value is shorter than that of a lower pH value at the specified operating conditions: $\sigma = 2.5$, $r = 1.0$, and $t = 24°C$. To check the constant composition, solution samples were withdrawn intermittently by using a syringe fitted with a 0.22-μm filter, and the calcium ion concentration was determined by the atomic absorption method. The evidence in Figure 4 shows that the concentration of calcium ion is nearly constant during the long period of operation for three runs. Alternatively, the constant composition of the solution can be controlled by using a calcium-ion electrode, as shown in Figure 5, which shows the constancy of hydrogen-ion concentration for the systems of r (concentration ratio of T_{CA}/T_{CO_3}) being less than 1.

Effects of operating variables on the polymorphism

A preliminary investigation of the factors that affect the polymorphism of calcium carbonate has been conducted by Tai et al. (1998), including solution pH, temperature, supersaturation, and initial concentration of component. In this study two more factors are considered and all the factors are systematically studied.

Solution pH is the most important factor as far as the polymorphism of calcium carbonate is concerned. Therefore, the percentage of polymorphs were plotted against solution pH as shown in Figure 6. For a fixed temperature ($t = 24°C$), su-

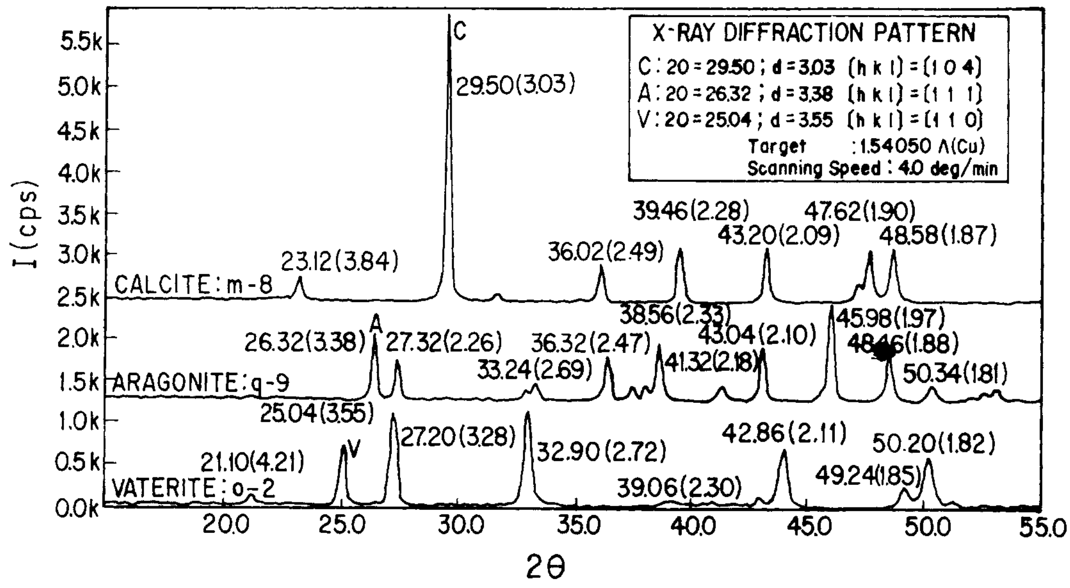

Figure 2. X-ray powder diffraction patterns of calcium carbonate.

persaturation ($\sigma = 5.5$), and concentration ratio ($r = 1.0$), vaterite is the major product in the pH range between 8.5 and 10.0; a similar result was reported by Kralj et al. (1990). The yields of aragonite and calcite increase with an increase in pH value. Aragonite shows a maximum at pH 11, and then drops to almost nothing at pH 12.5. Using an MSMPR crystallizer, Swinney et al. (1982) obtained high-purity aragonite, but at a pH around 10. Because the pH value is higher than 12, calcite is the dominant product. Wachi and Jones (1991) have confirmed this polymorph at high pH values.

Any change in any operating variable other than pH would change only part of the distribution curves shown in Figure 6. When σ decreases to 2.5, the distribution curves are similar to Figure 6. A further increase of σ to 8.0 causes the maximum yield of aragonite to drop to 60% and the yield of calcite to increase at the expense of vaterite production for pH values lower than 9.5. At low temperatures ($t = 7°C$), the aragonite was suppressed, yielding more calcite below pH 11, as indicated in Figure 7. On the other hand, nearly pure aragonite was produced at 58°C for a pH lower than 10.0, as shown in Figure 8. When the pH is greater than 12, the major product is still calcite, as in case of low temperature. The temperature effects are consistent with those reported by Wray and Daniels (1957) in a free-drift experiment. The change in concentration ratio of T_{CA}/T_{CO_3} does not change the shape of the distribution curves; for example, the maximum yield of aragonite shifts to a lower pH as the concentration ratio increases from 0.1 to 10, as shown in Figure 9.

Effects of ionic strength

The effects of ionic strength on the yield of polymorphs of calcium carbonate are shown in Table 1. The ionic strength was adjusted by the addition of sodium chloride, which is in-

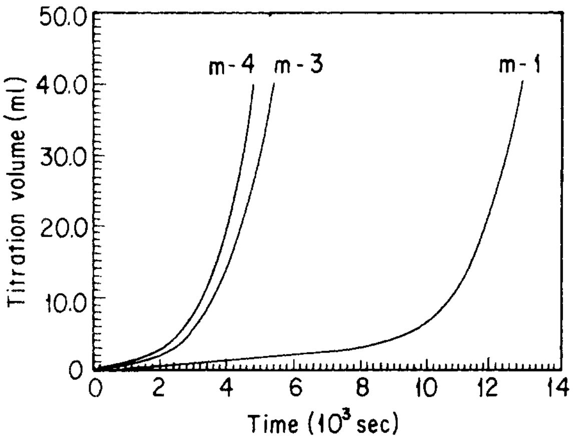

Figure 3. Titration curves in constant-composition operations of $CaCO_3$ precipitation at $\sigma = 2.5$, $r = 1.0$, $t = 24°C$.

$m-1$: pH = 8.5; $m-3$: pH = 9.5; $m-4$: pH = 10.0.

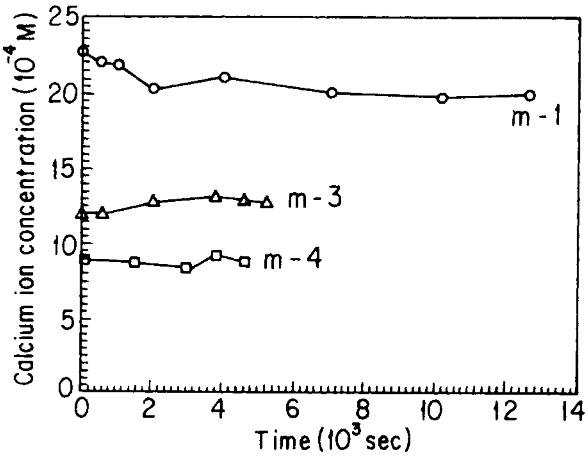

Figure 4. Concentration of calcium ion during constant-composition operations controlled by a pH-electrode at $\sigma = 2.5$, $r = 1.0$, $t = 24°C$.

$m-1$: pH = 8.5; $m-3$: pH = 9.5; $m-4$: pH = 10.0.

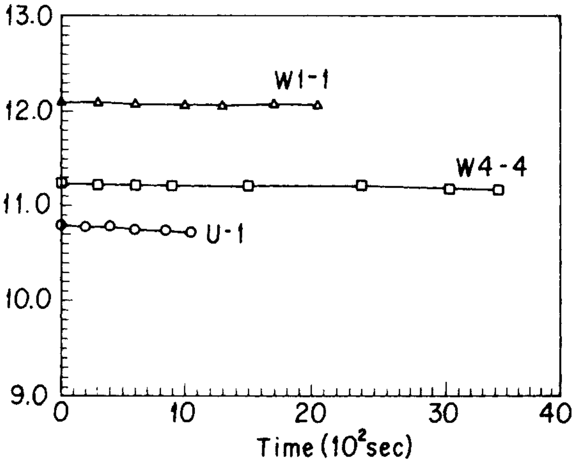

Figure 5. Solution pH in constant-composition operations controlled by a calcium-ion electrode at 24°C.

Run	pH	r	σ
$U-1$	10.80	0.6	5.0
$W4-4$	11.20	1.0	2.5
$W1-1$	12.10	0.1	5.5

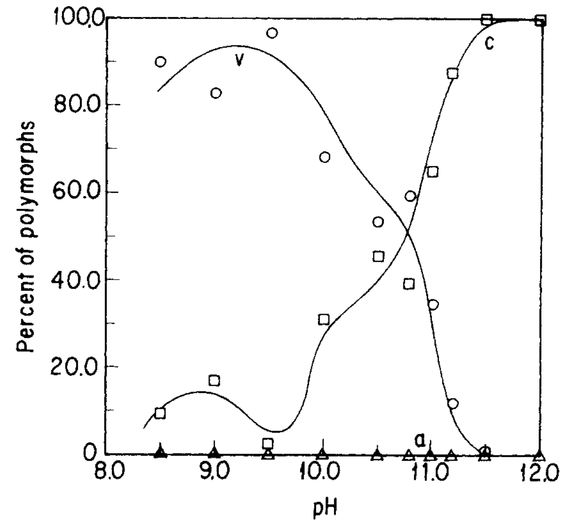

Figure 7. Percentage of $CaCO_3$ polymorphs at $t = 7°C$, $\sigma = 5.5$, $r = 1.0$.

○: vaterite; △: aragonite; □: calcite.

active in the polymorphic form (Söhnel and Mullin, 1982). An increase in ionic strength decreases the yield of calcite and increases the yield of aragonite for the conditions that favor the production of calcite. The effect of ionic strength is not significant for the operating conditions in favor of aragonite when the ionic strength is smaller than 0.0328 M; however, the yield increases for aragonite when the ionic strength is smaller than 0.0328 M; however, the yield increases for aragonite and decreases for vaterite and calcite when the ionic strength is raised to 0.1101 M. In both cases, the increase in the yield of aragonite is less than 20%. Although an increase in the yield of aragonite is observed at higher ionic strength, the highest yield of aragonite is about 84%, which is much less than that at high temperature. On the other hand, the effect of ionic strength is not significant for the operating conditions that favor the formation of vaterite. It can be concluded that ionic strength is not an effective factor that determines the polymorphic form of calcium carbonate as compared with the other factors investigated in this experiment.

Effects of additives

Three additives were investigated in this study: $MgCl_2$, $MnCl_2$, and KH_2PO_4. Generally, Mg^{2+} and Mn^{2+} will promote the formation of aragonite or calcite, depending on the

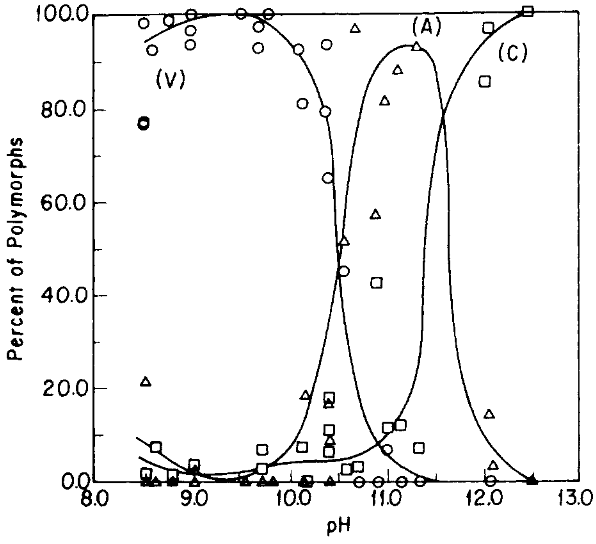

Figure 6. Effects of pH on the yield of $CaCO_3$ polymorphs at $t = 24°C$, $\sigma = 5.5$, $r = 1.0$.

○: vaterite; △: aragonite; □: calcite.

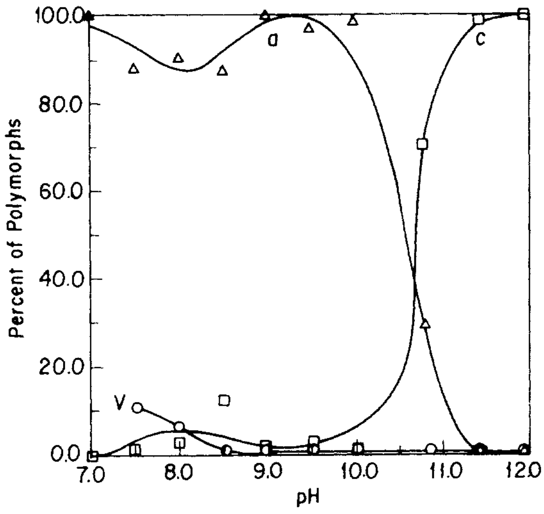

Figure 8. Percentage of $CaCO_3$ polymorphs at $t = 58°C$, $\sigma = 5.5$, $r = 1.0$.

○: vaterite; △: aragonite; □: calcite.

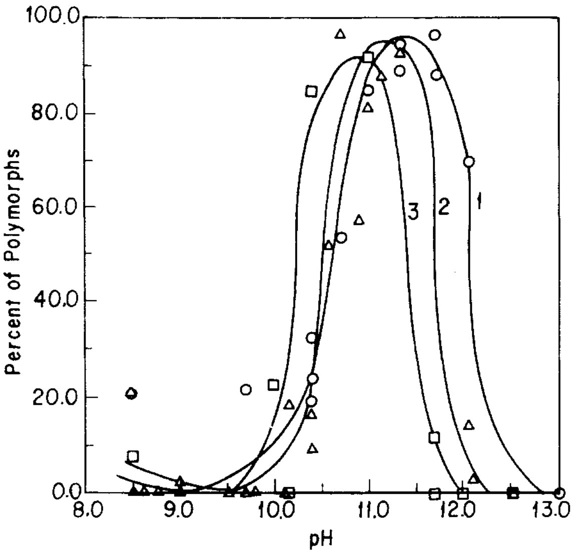

Figure 9. Effects of $R(T_{CA}/T_{CO_3})$ on the yield of aragonite at $\sigma = 5.5$, $t = 24°C$.

○: $r = 0.1$; △: $r = 1.0$; □: $r = 10$.

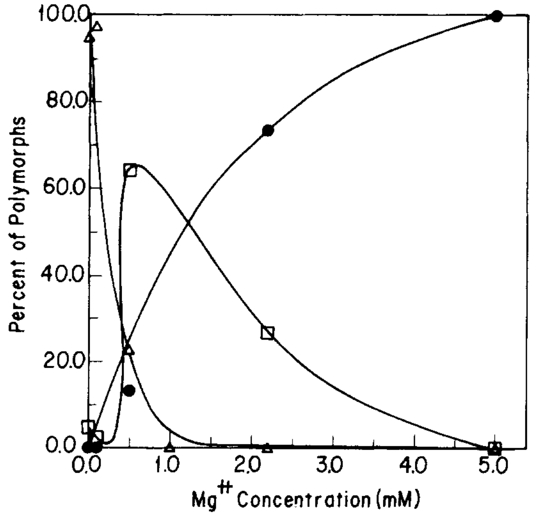

Figure 10. Effects of Mg^{2+} concentration on the yield of $CaCO_3$ polymorphs.

△: vaterite; ●: aragonite; □: calcite.

operating conditions and concentration of additives, whereas KH_2PO_4 increases the yield of calcite in all cases. Table 2 shows that the addition of $MgCl_2$ promotes the production of aragonite under the conditions in favor of either calcite or aragonite. Under the favorable conditions of vaterite, $MgCl_2$ suppressed the formation of vaterite and promoted the formation of calcite and aragonite first. Then, the calcite decreased quickly and the yield of aragonite increased continuously, as shown in Figure 10. At 5.0 mM of Mg^{2+}, nearly pure aragonite can be obtained at room temperature. Usually, pure aragonite is produced at temperatures above 70°C. The effects of $MnCl_2$ on the formation of polymorphs are similar to that of $MgCl_2$, but the aragonite does not dominate in a high concentration of Mn^{2+}, as shown in Figure 11. The effects of KH_2PO_4 are shown in Table 3. Nearly pure calcite is produced at pH 11.0 and 9.6 with a small amount of KH_2PO_4 added to the solution. Without additives, pure calcite is precipitated only when solution pH is higher than 12.

Table 1. Effects of Ionic Strength on the Yield of $CaCO_3$ Polymorphs

Operating Conditions	Ionic Strength (mol/L)	Vaterite (%)	Aragonite (%)	Calcite (%)
pH = 12.10 $\sigma = 4.0$,	0.0158	0	0	100
$r = 0.8$, $t = 20°C$	0.0265	0	8.17	91.83
In favor of calcite	0.0422	0	6.24	93.76
formation	0.1109	0	17.10	82.90
pH = 11.00, $\sigma = 5.5$,	0.0061	8.46	63.66	27.88
$r = 0.6$, $t = 24°C$	0.170	8.48	62.89	28.63
In favor of aragonite	0.0328	11.86	52.76	35.38
formation	0.1101	0	83.96	16.04
pH = 9.6, $\sigma = 4.0$,	0.0070	94.98	0	5.02
$r = 1.0$, $t = 20°C$	0.0178	97.95	0	2.05
In favor of vaterite	0.336	95.12	0	4.88
formation	0.0590	98.48	0	1.52
	0.1108	98.39	0	1.61

Table 2. Effects of $MgCl_2$ on the Yield of $CaCO_3$ Polymorphs

Operating Conditions	Mg^{2+} (mM)	Vaterite (%)	Aragonite (%)	Calcite (%)
pH = 12.0	0	0	0	100.00
$\sigma = 4.0$	0.2	0	2.4	97.60
$r = 0.8$	1.0	0	70.54	29.56
$t = 20°C$				
pH = 11.0	0	8.46	63.66	27.88
$\sigma = 5.5$	1.0	0	95.78	4.22
$r = 0.6$	2.0	0	100	0
$t = 24°C$				

Particle morphology of polymorphs

Particle morphology is used here to describe the overall external shape and appearance of particulate solids. During

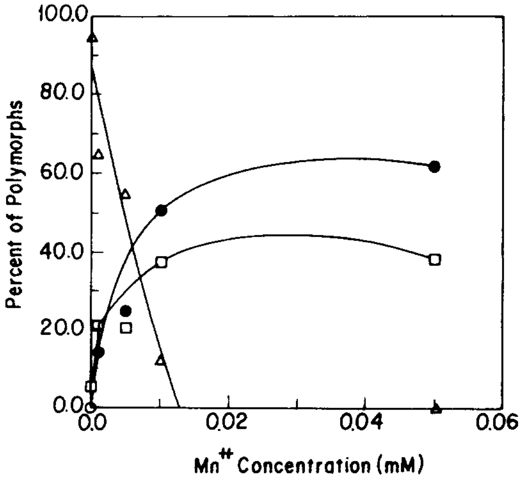

Figure 11. Effects of Mn^{2+} concentration on the yield of $CaCO_3$ polymorphs.

△: vaterite; ●: aragonite; □: calcite.

Table 3. Effects of KH_2PO_4 on the Yield of $CaCO_3$ Polymorphs

Operating Conditions	KH_2PO_4 (mM)	Vaterite (%)	Aragonite (%)	Calcite (%)
pH = 11.0	0	8.46	63.66	27.88
$\sigma = 5.5$	0.01	0	0	100
$r = 0.6$				
$t = 24°C$				
pH = 9.6	0	94.98	0	5.02
$\sigma = 4.0$	0.003	64.16	0	35.84
$r = 1.0$	0.010	0	0	100
$t = 20°C$	0.015	0	0	100

the course of the study of $CaCO_3$ polymorphism, different particle morphologies have been observed for the polymorphs of calcium carbonate.

Several calcite forms, such as rhombohedron, polycrystal, football-shape, and their agglomerates, were produced in this study. The well-known rhombohedron crystals precipitate at low supersaturation and a pH higher than 11; however, rhombohedra with hopper appear at high supersaturation ($\sigma = 98.0$) or with the addition of orthophosphate, as shown in Figure 12. Figure 13 shows the less common form of football-shaped calcite, which is produced at a high temperature and high supersaturation.

High-purity aragonites in a rosette form are produced at high temperatures or at room temperature with the addition of Mg^{2+}, as shown in Figure 14. For the operating conditions of Figure 14 without the addition of an additive, the major product is vaterite. At room temperature and a pH around 11, and with or without the addition of Mg^{2+}, twin rosette aragonite forms with a symmetry resembling a dumbbell (see Figure 15). When the operating temperature raises to 58°C, needle aragonites precipitate. This needle form of aragonite was reported by Xyla and Koutsoukos (1989).

Solution pH and temperature are the major factors that influence the vaterite morphology. Three crystal forms—spherulite, hexagonal-plate, and lettuce morphologies—are obtained at different operating conditions. As indicated in Figure 16, the spherulite form of vaterite was produced at lower pH (pH < 9.3) and below room temperature, while the hexagonal-plate form, as shown in Figure 17 was formed when the pH value increased to 9.6. The transformation from spherulite to hexagonal-plate with the pH change is similar to that reported by Kojima et al. (1992). The lettuce-shaped vaterite (Figure 18) appears at mild temperatures ($t = 40°C$) and pH 8.5, and was observed by Rojkowski and Garside (1992) at pH 8.0 using an MSMPR crystallizer.

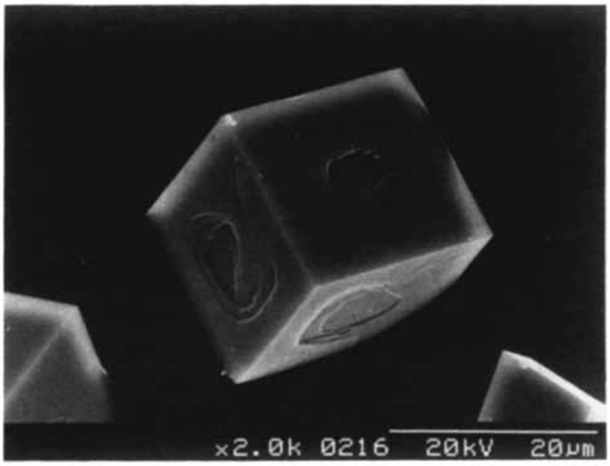

Figure 12. Rhombohedron calcite with hopper.
Run n-6: pH = 11.0; $\sigma = 8.0$; $r = 1.0$; $t = 24°C$.

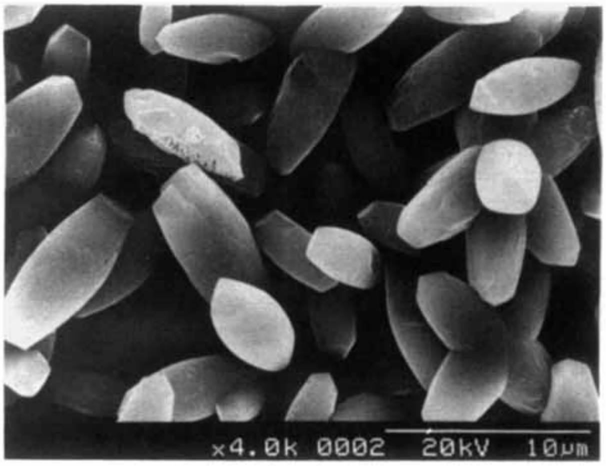

Figure 13. Football-shape calcite.
Run q-11: pH = 11.5; $\sigma = 5.5$; $r = 1.0$; $t = 58°C$.

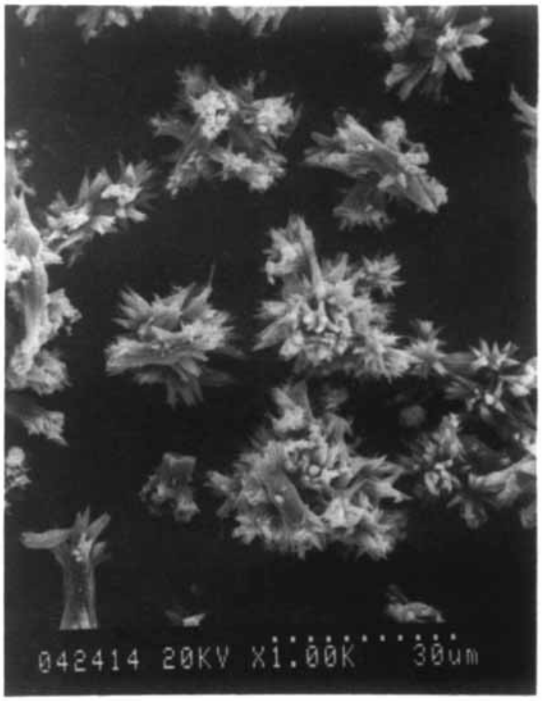

Figure 14. Rosette aragonite with 5 mM Mg^{2+} present in the solution.
Run v-a6: pH = 9.5; $\sigma = 4.0$; $r = 1.0$; $t = 20°C$.

Figure 15. Twin-rosette aragonite.
Run h-17: pH = 10.7; σ = 5.5; r = 1.0; t = 24°C.

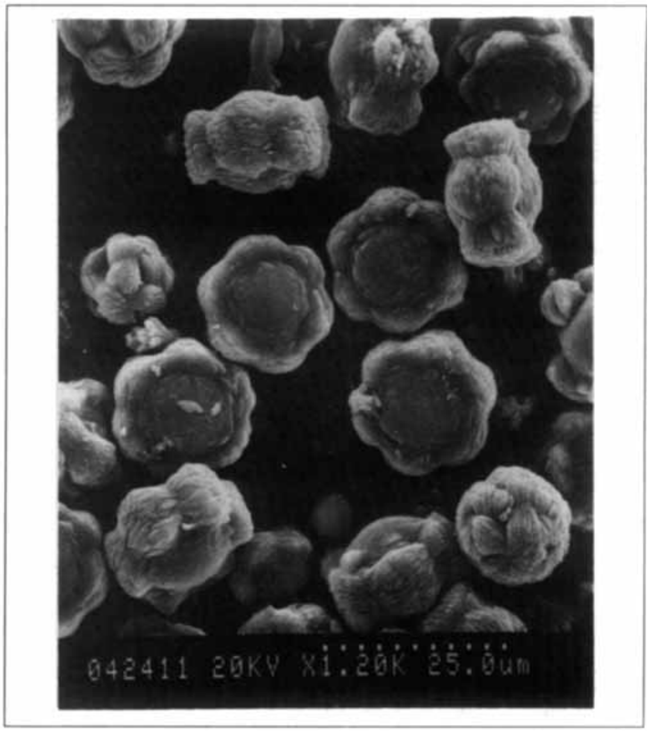

Figure 17. Hexagonal-plate vaterite.
Run v-2: pH = 9.6; σ = 4.0; r = 1.0; t = 20°C.

Conclusions

The constant-composition method is a useful tool in the study of polymorphism of calcium carbonate, because experiments can be designed to see the effects of one variable on the polymorphism while keeping other variables constant. The controlled variables are solution pH, temperature, supersaturation, concentration ratio of components, and concentration of additives.

Solution pH and temperature are the most important factors. At room temperature high-purity calcites and vaterites are obtained at a pH greater than 12 and a pH lower than 10, respectively, while the maximum yield of aragonite occurs around pH 11. At high temperatures, aragonites become the major product when the pH is below 11, but calcites still prevail at higher pH. The presence of magnesium and manganese ions favors the formation of aragonite or calcite, depending on the operating conditions, while orthophosphate favors calcite. The effects of the concentration ratio of the components and supersaturation are less significant as compared with other factors investigated in this study.

A nearly pure form or mixture of polymorphs is produced

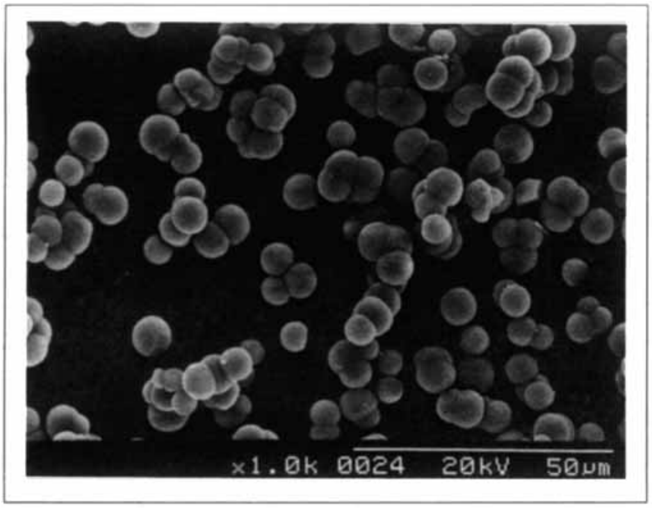

Figure 16. Spherical vaterite.
Run s-3: pH = 9.5; σ = 5.5; r = 1.0; t = 7°C.

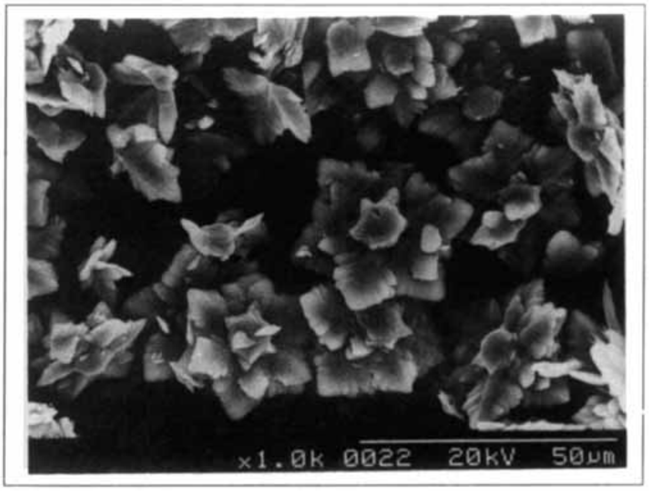

Figure 18. Lettuce-shaped vaterite.
Run p-1: pH = 8.5; σ = 5.5; r = 1.0; t = 40°C.

by adjusting the operating conditions. The operating conditions in the ranges studied can be identified for the predominant polymorphic form: pH higher than 12 for calcite; temperature higher than 58°C, but pH lower than 12 for aragonite; pH between 9.0 and 9.5 at room temperature and moderate supersaturation (see Figure 6) for vaterite. In addition various particle morphologies of $CaCO_3$ polymorphs have been observed, depending on the operating conditions: rhombohedron, polycrystal, and football-shape for calcite; rosette, twin rosette, and needle for aragonite; spherulite, hexagonal-plate, and lettuce-shape for vaterite. It seems that the important factors that affect the polymorphs and the shape of $CaCO_3$ crystal were under control in the experiment.

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Notation

C_i = concentration of species i, mol/L
T_{CA} = total concentration of calcium, M
T_{CO_3} = total concentration of carbonate, M

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