

The Precipitation of Calcium Carbonate¹

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The formation of calcium carbonate by chemical precipitation has been the subject of a number of investigations because of the commercial importance of this material in the pigment, sugar and paper industries. In the course of published researches, a few anomolous situations have arisen and much of the data has been treated only empirically. It is the purpose of the present study to investigate the precipitation of calcium carbonate in light of our present concepts concerning the formation of precipitates.

Calcium carbonate precipitates, under proper conditions, in one or more of three forms: calcite; aragonite; vaterite. Faivre has studied this precipitation process by mixing aqueous solutions of sodium carbonate and calcium chloride, with a view toward determining which form predominates as a function of temperature of formation (1). He reported that below 60° C. vaterite is always formed, but that this modification is very unstable and is rapidly transformed to calcite so that pure calcite can be separated after a reasonable aging period. He did succeed in isolating vaterite by rapid separation from an alcoholic precipitation medium. Faivre further reported that pure aragonite can be obtained at 60° C., while a calcite-aragonite mixture appears above 60° C. Lucas reported that both aragonite and vaterite revert to calcite unless kept dry (2). Noda confirmed the formation of aragonite at elevated temperatures (3). It may be noted that the function of temperature in determining the crystal form of precipitated calcium carbonate has been investigated thoroughly, but that little attention has been paid to the precipitation medium and time of aging and no attention to pH.

Spengler reported that in all cases a primary floccular substance is first formed which immediately begins transformation to one of the crystalline forms (4). Ephraim assumes the floccular material to be amorphous (5).

A number of industrial processes for the formation of fine particles of calcium carbonate have been reported, chiefly in the patent literature. In general, small particles have been obtained by some combination of the following: temperature below 40° C.; pH above 8; rapid addition of more concentrated reagent to more dilute one; digestion time as short as possible.

Experimental

The calcium carbonate samples were prepared by direct mixing of solutions of calcium chloride and sodium carbonate, each with the

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desired combination of conditions and concentrations. Temperature control was achieved with a water bath regulated within one-half degree of the desired temperature. A Beckman pH Meter was employed for all pH measurements. Electron microscope observations were made with an RCA type EMU instrument, and x-ray diffraction patterns were made with a Hayes instrument.

Each precipitate-suspension was centrifuged once and the supernatant decanted prior to electron microscope observation to rid each sample of dissolved material which would otherwise contaminate the crystals. Specimens were mounted on specially prepared formvar films

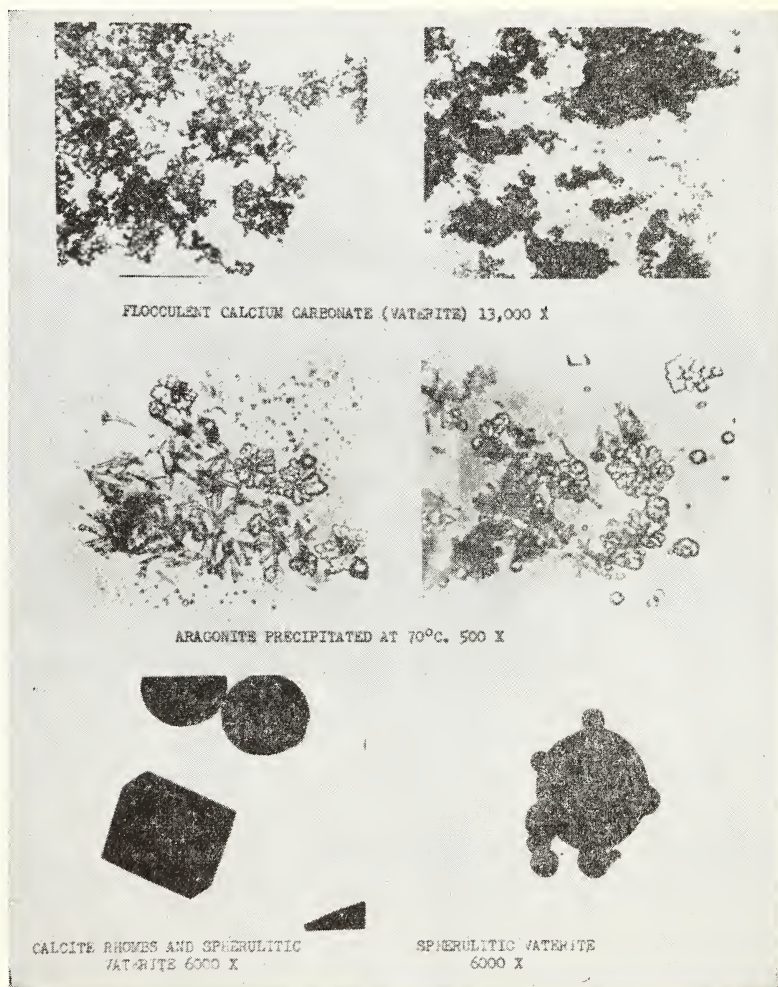


Fig. 1. Micrographs (middle row light micrographs; other electron micrographs)

which were in turn supported by standard 200-mesh nickel grids. The entire mounting procedure, from the time of mixing reagents to the time of completion of the mounting for final observation, took less than five minutes except, of course, in those cases when a controlled aging period was purposely introduced prior to mounting.

Results with Discussion

Crystal Form. The crystal form of precipitated calcium carbonate was investigated in so far as it is determined by the medium from which precipitated, the time of aging in the mother liquid, the pH at the time of precipitation and the temperature of formation from aqueous medium.

1. Medium from which precipitated. An alcoholic medium distinctly favored the formation of a flocculent material with only a trace of other forms. X-ray diffraction patterns of this material showed that it is not merely an amorphous material, but rather that it is finely divided crystalline vaterite. From water, calcite, calcite plus aragonite, aragonite, or calcite plus vaterite appeared, depending upon the temperature. Micrographs are shown in figure 1, while the x-ray data is summarized graphically in figure 2. The vaterite floc consists of chain-like units of varying length, each chain consisting of small circular particles, seemingly with less dense material holding them together. The small particles appear spherulitic.

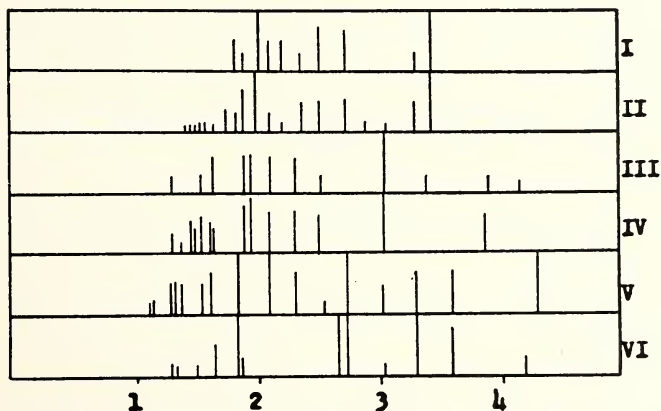


Fig. 2. The d-distances from x-ray diffraction data for the following: I. Precipitated calcium carbonate, needles; II. Aragonite, A.S.T.M. cards; III. Precipitated calcium carbonate, rhombs; IV. Calcite, A.S.T.M. cards; V. Vaterite, A.S.T.M. cards; VI. Precipitated calcium carbonate, flocculent.

2. Time of aging in the mother liquid. Aging in each case caused a growth of the crystals, but in no case was there any distinct change in form upon aging. Even vaterite spherulites, contrary to expectations based upon earlier published reports, were found to remain as spherulites rather than reverting to calcite rhombs. Aging of the alcohol-formed

floc did result in the appearance of a few rhombs, but the predominant tendency was definitely to retain a shape indicative of the same crystal form. (As stated above, a total elapsed time of nearly five minutes was required to complete the mounting procedure; the observed effects of longer aging periods indicate that likely no significant changes of crystal form could have occurred during that five minute period.) Thus all crystal forms appear to be quite stable in contact with the mother liquid.

3. pH at time of precipitation. The pH of the precipitation medium at the time of precipitation was adjusted to several values ranging from 7.4 to 11. The crystal form of the precipitated calcium carbonate was independent of the pH.

4. Temperature of formation from aqueous medium. At temperatures ranging from 8° C. to 50° C., the calcite rhomb is the dominant form, with lesser quantities of spherulitic vaterite appearing. The relative amount of vaterite was found to decrease as the temperature was increased, with no vaterite appearing above 50° C. At 55° C.

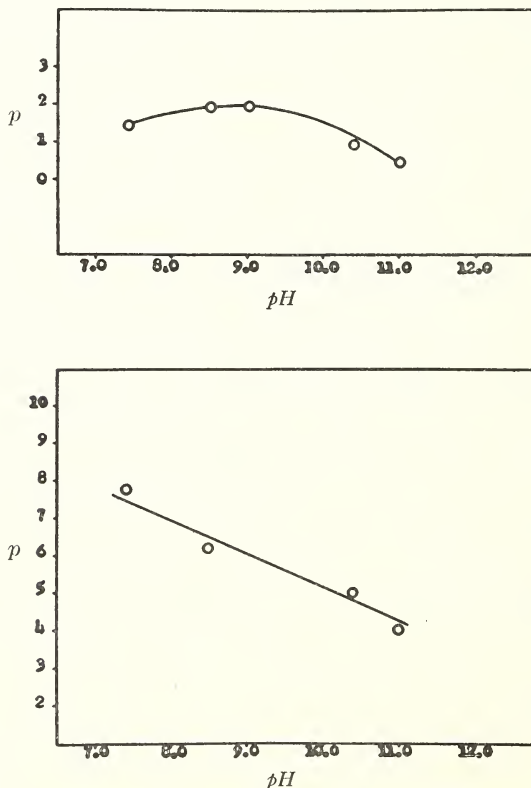


Fig. 3. Particle size as function of pH (top 5 min. size; bottom 30 min. size)

aragonite began to appear with calcite, either as bunches of strings (vigorous shaking) or as "cauliflowers" (slow mixing). Pure aragonite appeared at temperatures from 57° C. to 73° C., with a little calcite also appearing at still higher temperatures. As stated above, the role of temperature in determining the crystal form has been studied extensively elsewhere; these results are in essential agreement with previously published results with the additional identification of the flocculent material as vaterite.

Particle Size. Each particle size determination was made by measuring all the particles in the center region of the mounted specimen, covering about 15 openings of the 200-mesh supporting grid. About 250 to 300 particles were measured in each determination. Most measurements were made visually with the aid of graduations on the fluorescent viewing screen, although micrographs were taken periodically to check the measurements. The calibration of the electron microscope was made by observation of uniformly-sized polystyrene latex spheres supplied by courtesy of the Dow Chemical Company. The length of the longest side was taken as the size of the calcite rhomb, and the diameter as that of the spherulitic vaterite. The particle size was studied as a function of the pH of formation, of the time of aging in the mother liquid, and of the temperature of formation.

1. pH of formation. These results are shown graphically in figure 3. Because the pH would be expected to influence the solubility of calcium carbonate through the carbonate-bicarbonate equilibrium, and because the solubility would be expected to influence the rate of precipitation through the von Weimarn concepts, it should be expected that the particle size would be a function of the pH at the time of precipitation. It is noted that the five minute size vs. pH curve differs from that of the thirty minute one in that the former has a definite maximum within the pH range studied; this may be accounted for by the fact that the von Weimarn rate of precipitation is slower for the more soluble precipitates so that some of the precipitates measured rapidly after formation had not had time to reach a size which could be considered normal for those particular conditions. Therefore the thirty minute sizes may be taken as of more significance in determining the influence of pH upon particle size.

It is possible to calculate the influence of pH upon the solubility of the calcium carbonate, and then from the experimental data to observe the relationship between solubility and particle size. The solubility calculation may be summarized as follows.

Set up simultaneous equations—

$$6 \times 10^{-11} = \frac{(H^+)(CO_3^{=})}{(HCO_3^-)}$$

$$3 \times 10^{-7} = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)}$$

$$9 \times 10^{-9} = (Ca^{++})(CO_3^{=})$$

$$1 \times 10^{-14} = (H^+)(OH^-)$$

$$(H^+) + 2 \times 10^{-1} + \frac{(Ca^{++})}{2} = (OH^-) + \frac{(CO_3^{--})}{2} + 2 \times 10^{-3} + (HCO_3^-);$$

this series of five equations with six unknowns makes possible the determination of one of the unknowns, (Ca^{++}) , which is in reality the molar solubility of calcium carbonate, in terms of another, the (H^+) ; the results are as follows along with a tabulation of the thirty minute size data from figure 3:

pH	molar solubility	log mol. soly	size
7	7.6×10^{-5}	-4.12	7.9
8	7.6×10^{-6}	-5.12	7.0
9	7.7×10^{-7}	-6.11	6.0
10	9.7×10^{-8}	-7.01	5.2
11	3.1×10^{-8}	-7.51	4.2

It is apparent that the size of crystal is an inverse function of the log of the solubility,

$$\text{size} = \frac{k}{\log \text{ molar soly}},$$

in which the proportionality constant, k , is about -35 for this

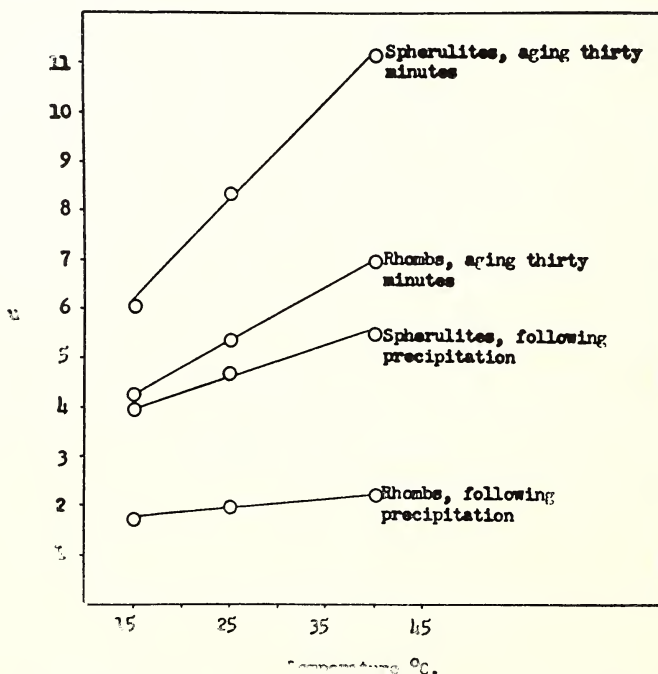


Fig. 4. Particle size as function of time of aging in mother liquid.

particular series. The von Weimarn concept states that the rate of precipitation is a function inversely of the solubility, rate $= \frac{Q}{S}$, Now these data show further that the size of crystal precipitated is an inverse function of the log of the solubility. It might seem that such a relationship could be determined with any one of a number of precipitates but such is seldom possible because a change in solubility is often accompanied by some sort of change in crystal form or at least in degree of perfection of the crystals. In the case of calcium carbonate, the form and shape and degree of perfection have just been shown to be independent of pH.

2. Time of aging in mother liquid. In every case studied, the particle size increased during aging in the mother liquid. A thirty minute period, in general caused an increase of 100% to 200% for the rhombs and an increase of 50% to 100% for the spherulites, each based upon the five minute size as reference, figure 4. This tendency is to be expected on the basis of Ostwald ripening concepts, a phenomenon often encountered, even though it is not as common as formerly thought.

3. Temperature of formation. The particle size of precipitated calcium carbonate, whether calcite rhombs or vaterite spherulites, was found to increase with rising temperature of precipitation. This appears at first to be contrary to expectations, because Seidell's solubility tables indicate a very definite decrease in solubility with rising temperature. An explanation may be based upon a consideration of the influence of temperature on the ionization constants of water and of carbonic acid. Qualitatively, the ionization of water increases as the temperature rises, thus increasing the H^+ ion concentration to complex more carbonate ions, in turn tending to offset any inherent solubility decrease. Calculations indicated that the increased complexing of carbonate ions is more than enough to offset any nominal decrease in solubility and thus is adequate to account for the observed phenomenon. However, the quantitative influence of temperature upon solubility product of calcium carbonate and upon ionization constants of carbonic acid do not appear well enough established to justify any more than a qualitative suggested explanation for the increase in particle size as the temperature is increased.

Summary

The precipitation of calcium carbonate has been studied with the aid of the electron microscope and x-ray diffraction to ascertain the effects of various conditioning factors upon the crystal form and the particle size of precipitate. Factors studied are the medium from which precipitated, the time of aging in contact with the mother liquid, the pH at the time of precipitation and the temperature of formation.

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