SOLUTION AND DEPOSITION OF CALCIUM CARBONATE IN A LABORATORY SITUATION IV

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Received June 20, 1980

This is a final report in a series of research investigations designed to determine the conditions necessary to attain rapid precipitation of $CaCO_3$ in the laboratory. It is shown that rapid formation of deposits is possible utilizing a decrease in pressure as limestone-laden waters emerge into the atmosphere.

Introduction

A tentative model for the formation of limestone, cavern development, and subsequent precipitation of stalactites, stalagmites, and dripstone in relation to the Flood has been reported.[1] Also experimental results were presented on the various conditions that could cause the rapid formation of $CaCO_3$ structures in the laboratory.[2-4]

A series of experiments and field observations on the conditions under which calcium carbonate ($CaCO_3$) can be deposited rapidly from solution in the laboratory are reported at this time. The principal variable investigated in this sequence is pressure difference. Rain or flood waters are subjected to pressure variations when moving through soil and limestone into caves. The acidic water (H_2O+CO_2) dissolves $CaCO_3$ as it flows through fissures in layers of limestone. When this calcium carbonate-laden water enters a cave it experiences a decrease in pressure causing precipitation of dissolved material. Such conditions are considered to be one of the chief mechanisms in the formation of cave deposits.[5]

Precipitation Experiments - Apparatus 1

The laboratory apparatus shown in Figure 1 was employed in the early tests. A 6 inch x 6 inch x 6 inch Plexiglas solution box was filled with crushed Beekmantown dolomite (used in all experiments) and sealed. Deionized water charged with CO_2 was allowed to flow into the solution box and drip down $CaCO_3$-coated strings suspended from the base. The water reservoir was positioned at a height such that the test pressure (P_t) varied depending upon the water level, from 1 to 1.4 atmospheres. The results obtained are shown in Table I.

The drip rate per string was monitored for the first 250 hours of the test. The time of drop formation and the amount of $CaCO_3$ precipitation was classified into four distinct groups as shown in Figure 2. The averaged results are tabulated in Table II.

The amount of precipitate increases as the drip rate decreases up to a maximum then decreases with a further slowdown of drip formation. Fast drop formation is a deterrent to precipitation. Possibly the "dwell time" of the drop on the string is not sufficient to allow the release of CO_2 so that $CaCO_3$ can precipitate.[6] An excessive drop "dwell time" may cause slow monocrystalline growth rather than rapid polycrystalline growth that occurs with faster moving drops.[7]

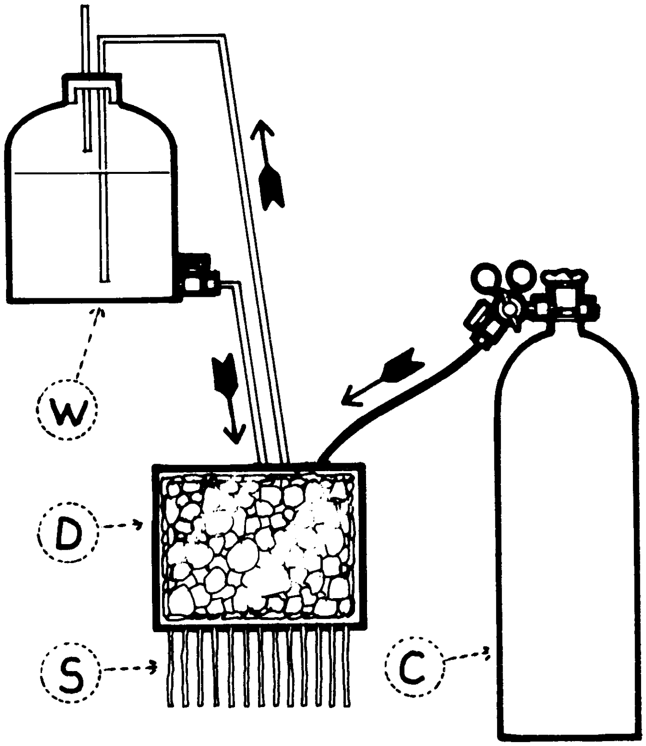

Figure 1. Small laboratory apparatus. The significance of the letters is as follows: C, carbon dioxide; D, dolomite; S, strings; W, water supply.

Another test was conducted using the same apparatus; and the results are recorded in Table III.

It was difficult to keep the box sealed against the internal pressure. Three trials were attempted before an experiment was completed. Also the small amount of dolomite in the box limited the amount of water-solid contact area which hindered the solution process. Therefore it was decided to construct another test rig.

Precipitation Experiments - Apparatus 2

A large cylindrical Plexiglas apparatus (Figure 3) was built to avoid as many "square" corners and edges as possible to eliminate leakage and to increase the amount of dolomite in the solution chamber. The sealed 1900 cubic inch apparatus contains three coated strings (A) inserted in the base. Fresh strings are mounted for

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Table I. Precipitation of $CaCO_3$ on Strings by Pressure Decrease - Run 1

String Number	*Mass of Deposition $CaCO_3$ (grams)*
1	0.3228
2	0.2481
3	0.2040
4	0.1771
5	0.1964
6	0.2434
7	0.2170
8	0.2542
9	0.2598
10	0.1949
11	0.2119
12	0.1740
total	2.7036g

Test Time - 500 hours 118 liters of water

Rate of Deposition - 0.401 $\frac{\text{grams of CaCO}_3}{\text{liter of water - year}}$

Table II. Effect of Drip Rate on Quantity of Precipitate Formed

Time Between Drops (seconds)	*Mass of Precipitate (grams/string)*
43	0.0514
90	0.0552
125	0.1317
215	0.1082

Table III. Precipitation of $CaCO_3$ on Strings by Pressure Decrease - Run 2

String Number	*Mass of $CaCO_3$ Deposition (grams)*
1	0.5565
2	0.1417
3	0.1975
4	0.1749
5	0.4202
6	0.3130
7	0.3781
8	0.4215
9	0.4288
10	0.2102
11	0.4657
12	0.2066
Ppt. at leak in solution box	0.0239
total	3.9386g

Test Time - 1314 hours 783 liters of water

Rate of Deposition - 0.0335 $\frac{\text{grams of CaCO}_3}{\text{liter of water - year}}$

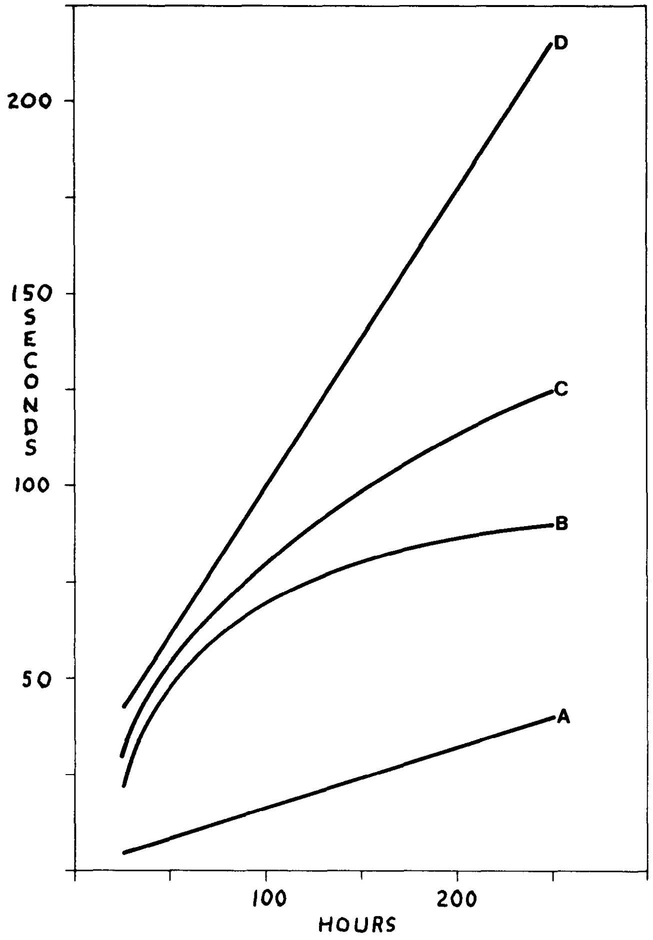

Figure 2. Drop formation time. Time between drops, in seconds, vs. test time, in hours. The different curves show the results for different strings, as follows: A: strings 4, 5, 8, and 11, drop time at 250 hours, 35-50 seconds. B: strings 2, 6, 7, and 10, drop time at 250 hours, 80-100 seconds. C: strings 1 and 3, drop time at 250 hours, 120-130 seconds. D: strings 9 and 12, drop time at 250 hours, 210-220 seconds.

each run. A hole (B) was drilled in the side of the container so that water with dissolved dolomite could trickle down the outside, precipitating $CaCO_3$. The water leaving the strings dropped onto a glass plate, then into a container. The collected exit water was recycled through the apparatus. Since natural water may travel considerable distance through limestone before entering a cave,[8] the recycled run-off water will contact more dolomite surfaces allowing a more realistic solution time.

Gas was periodically emitted into the solution chamber rather than allowing a continual flow as had been done in previous experiments to prevent the formation of an excessively acid solution which would hinder precipitation. Information collected in natural caves (Appendix I) indicates a slightly basic ($pH \approx 8$) drip solution at active precipitation sites. The results of the first run in the new apparatus are tabulated in Table IV.

A second trial was conducted and the results are shown in Table V.

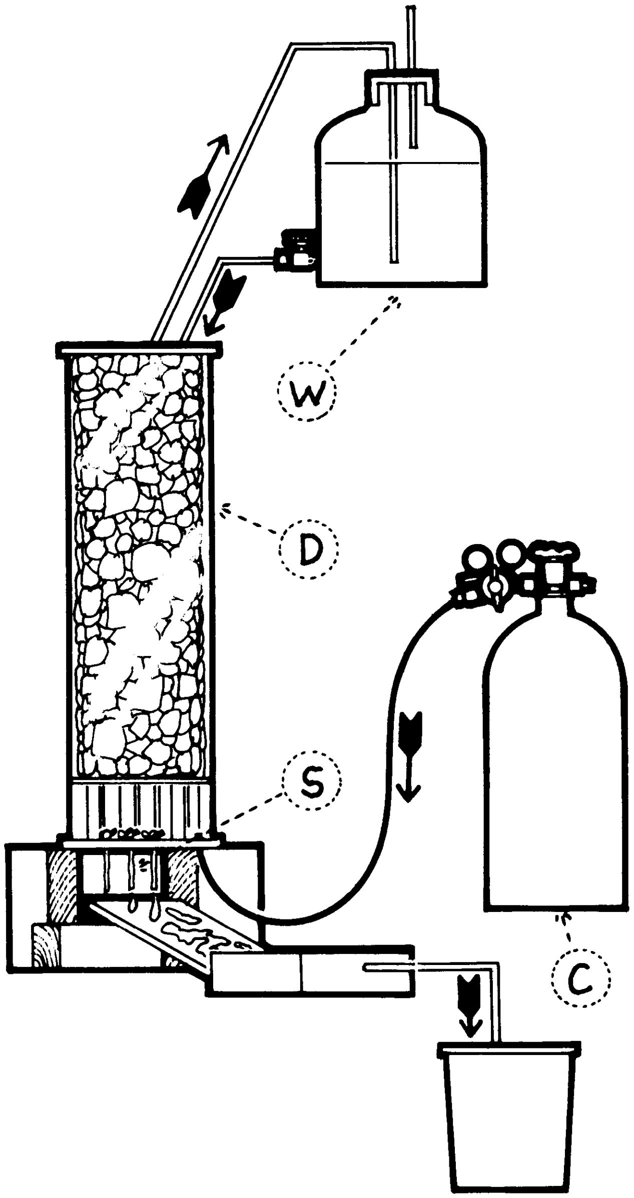

Figure 3. Large laboratory apparatus. The significance of the letters is as follows: C, carbon dioxide; D, dolomite; S, strings; W, water supply.

X-Ray Diffraction Studies

An x-ray diffraction analysis of precipitates formed in all of these experiments revealed that crystalline form of the $CaCO_3$ is calcite.

Initiation of Precipitation Tests

The onset of precipitation in all experiments does not occur until a certain "incubation" time (about 400 hours) has passed where no apparent precipitation takes place. After this time the precipitate becomes obvious and growth is visible.

The lag time-to-precipitation phenomena was investigated as follows. High purity reprecipitated $CaCO_3$ was placed into a liter of deionized water, and CO_2 was bubbled through the stirred mixture. The system was maintained for three days before stirring was ceased. At that time the undissolved calcium carbonate was allowed to settle and 500 ml of clear solution was decanted into a clean beaker. To encourage the removal of dissolved CO_2 the solution was again agitated with a magnetic stirrer. As shown in Figure 4, the pH increased slowly and leveled off at a value of 8.27. No precipitate was observed after three hours. The solution was then checked after 19 hours and found to have a pH of 8.15. $CaCO_3$ (calcite) had precipitated on the bottom and sides of the beaker. Most of the precipitate except for a small amount that had settled to the bottom of the container could not be washed away; it had to be removed by mechanical scraping. The same experiment was repeated using a known amount of limestone as an aggregate. After precipitation occurred the solid mass was dried and weighed. The limestone had gained 0.27 grams of adherent precipitate.

Table IV. Precipitation of $CaCO_3$ on Strings By Pressure Decrease - Run 3

String Number	*Mass of Deposited $CaCO_3$ (grams)*
1	0.0353
2	0.0435
3	0.4855
hole (B)	0.1803
glass plate	9.9110
	total 10.6556g

Test Time - 600 hours
157 liters of "fresh" water
315 liters of recycled water
472 liters total

Rate of Deposition - 0.330 $\frac{\text{grams of CaCO}_3}{\text{liter of water - year}}$

Table V. Precipitation of $CaCO_3$ on Strings By Pressure Decrease - Run 4

String Number	*Mass of Deposited $CaCO_3$ (grams)*
1	0.8222
2	0.6035
3	0.3622
hole (B)	1.1972
glass plate	9.8583
	total 12.8434g

Test Time - 600 hours
60 liters of "fresh" water
131 liters of recycled water
191 liters total

Rate of Deposition - 0.982 $\frac{\text{grams of CaCO}_3}{\text{liter of water - year}}$

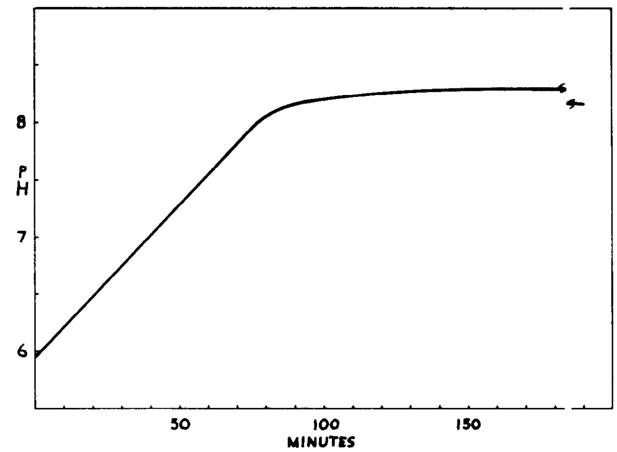

Figure 4. pH increase with time - calcium carbonate solution. Times in minutes, except that the mark after the break indicates 19 hours.

As explained, there is a time lag between the start of the experiment and the initiation of calcite precipitation. The lag may be due to time necessary to allow the removal of CO_2 from solution or the time necessary to supersaturate the solution with $CaCO_3$ before solid nuclei of the precipitating compound will become stable. Once precipitation occurs, it appears that the great majority of the deposit adheres to an existing solid surface. It is tempting to speculate on the role of fossil material as an aggregate medium for the deposition of sedimentary beds of limestone during the Flood similar to the function of gravel or stone aggregate in the hardening of Portland cement. Also, it is possible that falling or moving drops in a cave need to be exposed to the cave atmosphere or surfaces for a sufficient time to allow for stalactite and stalagmite formation because of the time lag before precipitation.

Conclusions

The results presented in this study indicate that a pressure loss in dripping water can produce rapid precipitation of $CaCO_3$ in the laboratory. Since 75-90% of the deposit is found on the glass plate, either the longer drop travel distance or the force exerted when a falling drop collides with a solid surface encourage precipitation. Also the rate of drop formation is another controlling factor in the amount of precipitate formed on the strings. Tentatively it appears that an optimum rate of flow down a surface yields a maximum amount of deposited $CaCO_3$.

In previous experiments it has been shown that temperature differences, as well as chemical composition differences in the solution and atmosphere, affect the amount of precipitate. Therefore it is concluded that large masses of $CaCO_3$ can be deposited rapidly under proper conditions.

Acknowledgements

The authors gratefully acknowledge the receipt of grants from the Creation Research Society for several years. These grants helped to finance part of the work.

Also the authors appreciate the help of other students at Bob Jones University in this phase of the study: Richard Mowrey, James Harper, and Carol Brumbalow.

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Appendix I Cave Observations

At the kind invitation of Mr. Richard Lambert, the research team visited four caverns in the Riverton, West Virginia area on December 2, 1978. Several measurements were made in various caves, particularly at the sites of actively growing stalactites and stalagmites. A synopsis of the results is given below.

Seneca Caverns - a commercial cave
- A. First large room just inside commercial entrance
  pH of water - slightly basic
  temperature - 56° F
  relative humidity 99%
- B. Several active sites throughout cave
  pH of water - slightly basic
  temperature variation - 51-55° F
  relative humidity variation - 89-99%

Stratosphere Balloon - very dry cave populated with hibernating bats
- A. Large formation at end of "phreatic tube"
  temperature - 53° F
  relative humidity - 99%
- B. Area near the wall of "phreatic tube"
  temperature - 62° F
  relative humidity - 61%

Ruddle Cave - contains many active areas
- A. Large inactive formation
  relative humidity - 98%
- B. Active soda straw site
  relative humidity - 100%
- C. Main room at end of "phreatic tube" with many helictite formations
  relative humidity - 47%

Appendix II Rapidly-Growing Structures in Caves

Examples of quickly-developing structures in various active caves can be documented (see the literature cited

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