DEPOSITION OF CALCIUM CARBONATE IN A LABORATORY SITUATION

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This account is an interim report. The purpose of the work is to investigate experimentally, under laboratory conditions, the precipitation of calcium carbonate dissolved in water. Such information is important to interpretations of dripstone formations, in caves and elsewhere, with regard to the age of the formations.

Experimental Rig

Figure 1 shows the experimental rig used in dissolution and later precipitation of calcium carbonate.

Tap water and carbon dioxide are brought into a box containing limestone chips. A magnetic stirrer is used to circulate the water and gas throughout the solution box (6" X 6" X 6" plastic). An exit tube near the top of this box is used to drain off the carbonate laden water into a precipitation box (6" X 6" X 6" plastic). Holes in the bottom of the precipitation box are filled with strings as shown. The water drips downward along the strings depositing calcium carbonate. A fan is used to blow air on the strings.

Humidity

The atmosphere around the strings is fairly humid since water is kept in the bucket on which the precipitation box is supported. Also the general atmospheric conditions in the Greenville area are rather humid so that very little evaporation takes place as the water flows down the strings. Also the drip rate is rapid enough to prevent extensive evaporation.

String Preparation

It is necessary to treat the strings used in the precipitation box so that they are similar chemically to material found on the roof of caves. Most commercial string is coated with materials to prevent deterioration. String coatings would resist any chemical action such as precipitation and is not suitable to use as is.

Lengths of string are steamed in glacial acetic acid for 20 minutes. The string is then placed in a flask containing powdered limestone and water. CO_2 is run through this mixture. The strings become impregnated with particles of $CaCO_3$ by this action.

Qualitative Solution Test

Early in the research program it was decided to determine how certain solutions under identical conditions were capable of dissolving limestone. Chunks of limestone were exposed to the following solutions for 12 hours:

1. tap water + CO_2
2. tap water + CO_2 + 5% NaCl
3. tap water + CO_2 + 1% acetic acid

The following amounts of $CaCO_3$ were dissolved by the test solutions:

1. 0.1040 g/100 ml of H_2O
2. 0.5393 g/100 ml of H_2O
3. 0.4019 g/100 ml of H_2O

Solution 1 can be considered similar to normal surface water that has percolated through the soil to a limestone layer. Solution 2 is a postulate type of Flood water high in NaCl that would have receded off the earth through recently consolidated limestone. Solution 3 is another postulated type of Flood water high in humic acid because of the decay of many living organisms killed by the Flood waters and collected in one place above recently consolidated limestone.

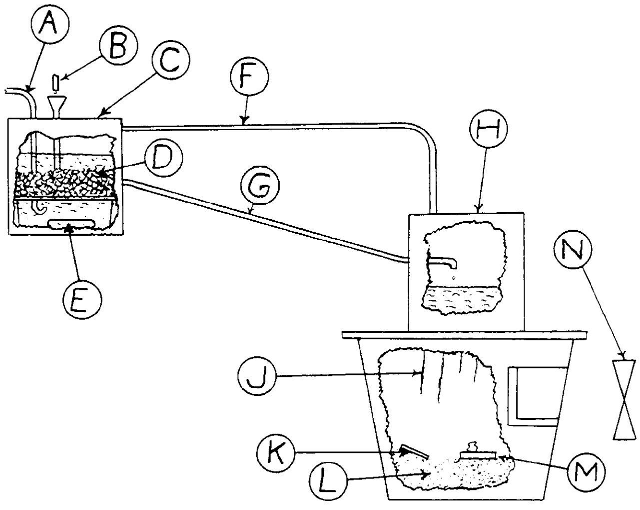

Figure 1. This shows the essentials of the arrangement of the experiment on the deposition of dripstone. The letters indicate the various parts or functions, as follows: A, carbon dioxide input; B, water input; C, rock box; D, limestone rocks; E, magnetic stirrer bar; F, carbon dioxide hose; G, hose for carbon dioxide, water, and dissolved limestone; H, string, or precipitation box; J, strings; K, glass plates; L, sand; M, rock (resting on a slab); N, fan.

Quantitative Tests

A 700 hour test was conducted on the deposition of dissolved limestone from a supposed natural rain water solution. The results of this run are shown in Table 1.

Table I. The deposition of limestone from a solution intended to simulate that formed by natural rain water.

String	Length (cm)	Weight of deposited $CaCO_3$ (g)	Deposition per cm of string
1	15.2	0.1725	0.01135
2	38.1	0.1975	0.005184
3	20.5	0.01510	0.0007365
4	14.4	0.4132	0.02871
5	17.1	0.1259	0.007362
6	9.9	0.1724	0.01741
7	17.8	0.2001	0.01124
8	16.3	0.1178	0.007224
9	7.2	0.1183	0.01643
10	10.4	0.2634	0.02533
		average: 0.17964 g	average: 0.0130979 g per cm

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Table II. The deposition of limestone from water containing dissolved CO_2 and 5% NaCl.

String	Length (cm)	Weight of deposited $CaCO_3$ (g)	Deposition per cm of string
1	14.0	0.3727	0.02662
2	14.6	0.3612	0.02474
3	16.3	0.4311	0.02645
4	20.8	0.6466	0.03109
5	9.2	0.2659	0.02890
6	8.9	0.2336	0.02625
7	17.8	0.4215	0.02368
8	9.4	0.3423	0.03641
9	22.6	0.4707	0.02083
10	11.8	0.2863	0.02426
11	15.0	0.3388	0.02259
12	15.1	0.2847	0.01885
		average: 0.3713 g	average: 0.02589 g per cm

Considering a density of deposited calcite of 2.70 g/cm^3 this corresponds to a volume of deposition of 0.83 cm^3 of calcite/year.

A 500 hour test was conducted on the deposition of dissolved limestone from a solution of tap water, CO_2, and 5% NaCl. The results of this run are shown in Table 2.

This corresponds to a volume deposition of 2.41 cm^3 of calcite/year. A total of 209 liters of saline solution were used in this test. The total amount of deposited $CaCO_3$ on the strings was 0.214 g/l of solution. $CaCO_3$ deposits all along the experimental system in the plastic box, outside the plastic box, and below the plastic box. Colloidal particles of clay often formed as ooze-like mud in caves was found in abundance in and under the experimental rig. The equipment is shut down every 100 hours to allow the strings to dry.

In the test where the saline solution was used, the strings were washed several times to insure the removal of any encrusted salt. The strings were always dried completely before weighing.

Chemical Analysis of Solutions

The solutions were analyzed periodically in the solution and string boxes to determine how much limestone wa actually being dissolved. The method employed was a pH end point titration.[1] The following results were obtained in the experiment using tap water plus CO_2, as shown in Tables 3 and 4.

Tables III, IV, and V. The results of analyses of the solutions in the solution box and the string box. The concentrations of HCO_3, CO_2, and $CaCO_3$ are given in mg/1. Table III gives the results of tests on the solution in the string box, Table IV on the solution in the solution, or rock, box, and Table V more results from the string box.

TABLE III

pH	HCO_3	CO_2	$CaCO_3$
6.10	671	1108	550
6.15	729	826	598
6.35	746	553	612

TABLE IV

pH	HCO_3	CO_2	$CaCO_3$
5.9	672	1354	551
5.9	704	1418	577

TABLE V

pH	HCO_3	CO_2	$CaCO_3$
6.25	824	742	676
6.25	918	826	753
6.35	951	680	780

Conclusions

As can be seen by the experimental results, massive precipitation of $CaCO_3$ is possible under laboratory conditions.

Several runs need to be made under similar conditions to verify results.

The data from the saline water experiment is more reliable than that from the tap water experiment. The latter was the first successful run, and there were still some "bugs" in the equipment. Several students were involved in the work, which consequently had to be started and stopped a number of times. The experiment with the saline water was conducted by one person and was not interrupted by any malfunctioning of the equipment.

We believe that it has been shown that the formation of dripstone can be investigated in the laboratory. More work needs to be done to investigate the effects of the several variables which are involved.

This work was supported, in part, by a grant from the Creation Research Society.

Reference

[1] Techniques of water-resource investigations of the United States Geological Survey–methods for collection and analysis of water samples for dissolved minerals and gases. 1970. Book 5, Chapter A1, U. S. Government Printing Office Stock Number 2401-1015, p. 41.